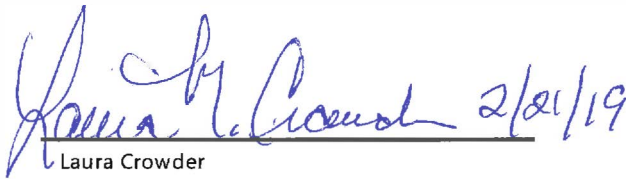


**EPA Office of Research and Development  
National Exposure Research Laboratory  
Research Triangle Park, NC**

**Project Study Plan**

**Targeted and Non-targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) In Air  
Emission Control Devices for the West Virginia Department of Air Quality (WVDAQ)**

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# 1 Problem Definition

## 1.1 Background

The West Virginia Division of Air Quality (WVDAQ) through EPA Region 3 has requested the assistance of specialized expertise within EPA's Office of Research and Development (ORD) to assist with sampling and analysis of per- and polyfluoroalkyl substances (PFAS) air emissions that may be produced at the Chemours facility in Washington, West Virginia. There is concern that emissions may potentially contaminate surface and groundwater in the surrounding area.

WVDAQ is attempting to identify and speciate various per- and polyfluoroalkyl substances (PFAS) compounds that may be generated at the Chemours facility from the Fluoropolymers production area and are emitted into surrounding environmental media through air. WVDAQ is particularly interested in quantifying the specific PFAS compounds, C3 dimer acid (HFPO-DA) (also known as "GenX"), Perfluorinated octanoic acid (PFOA) (also known as C8), and heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether, hereafter referred to as fluoroether (E-1), as well as to identify other PFAS that may occur within the facility.

There are a number of limitations in laboratory and sampling methods that limits characterization of a broader suite of PFAS compounds. Laboratory analytical barriers currently include:

- 1) commercial laboratory analytical limitations for handling more complex sample matrices;
- 2) unknown nature of many PFAS compounds because they are proprietary, manufacturing byproducts or degradation compounds contained in manufactured products and by products; and
- 3) lack of expertise and experience associated with advanced fluorochemistry and fate and transport properties. Sampling barriers include appropriate sampling approaches for comprehensive emissions sampling for PFAS compounds.

Chemours conducted emissions sampling in August and November 2018 to assess scrubber performance in reducing PFAS emissions. WVDAQ would like to use sample analysis results to evaluate the effectiveness of the facility's control devices to reduce emissions within the Fluoropolymers process to the extent possible. WVDAQ would also like to estimate PFAS emissions from the facility stacks based on a more comprehensive identification of PFAS compounds that may be present in emissions. Chemours has offered to provide the WVDAQ with split samples from the emission sampling.

Scientists in ORD's National Exposure Research Laboratory (NERL) and National Risk Management Research Laboratory (NRMRL) will be supporting WVDAQ's request by applying expertise in high resolution mass spectrometry and experience gained in assessing PFAS compounds in complex mixtures. ORD will analyze samples from the Chemours stack tests for a suite of PFAS compounds, including the three identified by WVDAQ that are of most interest.

WVDAQ seeks to use information generated at the Chemours facility to:

1. Quantify the amount of C3 Dimer Acid (GenX), PFOA, and E-1 in samples collected in MM-0010 trains to represent specific emission points within the Fluoropolymer manufacturing area;
2. Determine what additional PFAS are being emitted and their relative quantity in relation to the C3 Dimer Acid (GenX);
3. Determine the control efficiencies of current air pollution control devices used at the Chemours facility to reduce C3 Dimer Acid, PFOA, and E-1. PFAS of particular interest are HFPO-DA and PFOA although a comprehensive assessment of PFAS will be of value.
4. Understand the relative concentration of fluorinated compounds generated when emitting PFAS to the air;
5. Provide an independent comparison of analytical results reported by Chemours/contractors.

## 1.2 Project Overview

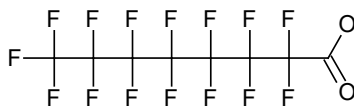
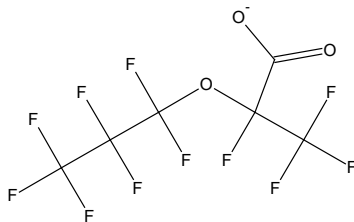
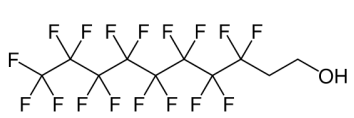
Chemours is conducting stack testing at their facility in Washington, WV associated with commercial use of PFAS. Chemours contracted with Weston Solutions (emissions sampling) and TestAmerica (sample analysis) to collect samples from the air emission control systems in August and November 2018 using Modified Method 0010 (MM-0010) sampling train protocols. TestAmerica extracted and created splits of the samples collected during testing. WVDAQ will coordinate the transfer of the methanol extract splits from Chemours/TestAmerica to ORD.

ORD principal investigators will apply HPLC/Tandem Mass Spectrometry to identify and quantify PFAS compounds in the samples provided. ORD has developed standards to perform targeted analysis to fully quantitate the concentrations of 24 PFAS for which we have standards. ORD will use complementary high-resolution MS to conduct non-targeted analysis (NTA) to identify and semi-quantify additional PFAS compounds in the liquid extracts that are amenable to LC/MS analysis using suspect screening and non-targeted methods.

WVDAQ has specific interest in PFOA and HFPO-DA (GenX) whose concentrations have been previously quantified by TestAmerica (Table 1). *Note that ORD is not currently able to evaluate the concentrations of fluoroether E-1 as requested by WVDAQ.* However, ORD is experimenting with methods to detect fluoroether using GC-MS and may add E-1 to the analysis if possible.

WVDAQ will work with ORD to compare results in the liquid extracts taking into account differences in analysis methods and holding times.

**Table 1. Priority analytes of interest for WVDAQ for targeted analysis.**

Short Name	Chemical Name	Formula	CAS no.	Monoisotopic Mass (Da)	Structure
PFOA	Perfluorooctanoic Acid	$C_8HF_{15}O_2$	335-67-1	413.9737	
HFPO-DA (GenX)	Hexafluoropropylene oxide dimer acid	$C_6HF_{11}O_3$	13252-13-6	329.9750	
E-1	Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether	$C_5HF_{11}O$	3330-15-2	286.044	

Once laboratory analyses of the liquid extracts are completed, WVDAQ and ORD will work together to consider ancillary sampling and sample processing data to estimate air emissions and control device effectiveness. The ability to do this will depend on the availability of critical testing information, such as total liquid volumes and gaseous sample volumes obtained during the stack testing events. ORD will work with WVDAQ to identify what information is needed and WVDAQ will be responsible for obtaining that information from Chemours and/or their contractors. This study plan will be updated with details of the air emission analysis methods once the necessary information is obtained.

## 2 Project Implementation

### 2.1 Project Responsibilities

Project participants from WVDAQ, Region 3, and ORD and their responsibilities are listed in Table 2.

**Table 2. Project participants, roles and responsibilities and distribution list.**

Project Personnel	Role	Responsibility
Regina Poeske	EPA Region 3 science liaison. Project point of Contact (POC)	Provide overall project coordination between WVDAQ, ORD, and Region 3/5 including convening meetings and communicating project results to WVDEP and R3/R5 constituents
Laura Crowder WV DAQ Director	WV DAQ Director and Point of Contact (POC)	Oversee and coordinate overall WVDAQ efforts, serve as key WVDAQ contact for R3 and ORD, direct communication of results within WV
Rebecca Johnson Compliance & Enforcement	WV DAQ Project Coordinator	Assist with overall project coordination and communication within WVDAQ work group
Mike Egnor	WV DAQ Facility expert	Assist with project scope and act as facility expert and contact
Richard Fenton	WVDAQ Stack Test Coordinator	Assist with project scope, testing plan and analysis of results
Timothy Buckley	EPA ORD/EMMD Coordinator ORD Point of Contact (POC)	Coordinate project discussions between EMMD, R3 and WVDEP
Mark Strynar	EPA ORD Principal Investigator	LC/MS Analysis
Jeff Ryan	EPA ORD Principal Investigator	Advise project on air sampling and emission estimates
John H. Offenber	EPA ORD Principal Investigator	Overall project development
Linda George	EPA ORD Principal Investigator	GC-MS &/or GC-ToF-MS analysis
Brian Gullett	EPA ORD/AEMD Coordinator	Coordinate project discussions between ORD's AEMD, R3 and WVDAQ
Myriam Medina-Vera	EPA NERL/EMMD/PHCB Branch Chief	EPA NERL/EMMD/PHCB Project laboratory oversight and approval
Sania W. Tong Argao	EPA ORD/EMMD QA Manager	Advises on QA requirements, reviews and approves project QAPP and associated SOPs; Conducts data reviews.
Kate Sullivan	EPA ORD/NERL IO	Project support & documentation management

## 2.2 Sampling Plan

The Chemours facility in Washington, WV conducted stack emissions testing in August 2018. Chemours has contracted with Weston (sampling) and TestAmerica (analytical) to conduct testing in the Fluoropolymers manufacturing area to quantify the amount of specific PFAS compounds (HFPO-DA, PFOA, E-1) and their degradation products that may be emitted to the air. Chemours completed stack testing using standard MM-0010 trains (Methods provided in Appendix A). Chemours conducted additional testing using the same methods within the Fluoropolymers area during the week of November 5, 2018.

### MM-0010 Stack Sampling

Emission tests were conducted by Chemours contractors using MM-0010 trains from multiple areas within the facility during the 2 testing events. Each sampling run at an emission control point included two MM-0010 trains deployed simultaneously at the inlet and outlet of the scrubber for the purpose of determining scrubber optimization and process emission identification.

Four extracted samples are produced from each MM-0010 sample train:

- Front-Half Composite—consisting of a particulate filter, and a probe, nozzle and front portion of the filter holder bell housing glassware solvent rinses,
- Back-Half Composite—consisting of an XAD-2 resin module, and the back portion of the filter holder bell housing with connecting glassware solvent rinses,
- Condensate and Impinger Contents—consisting of the D.I. Water content used to initially charge the impingers and Condensate collected during the sampling run.
- Breakthrough XAD-2 Resin Tube—consisting of a standard XAD-2 module placed behind the Condensate Impingers as a final quality assurance indicator of the lack of breakthrough of the HFPO-DA through the sampling train

TestAmerica extracted samples from the MM-0010 samples using methanol and analyzed them in their laboratory in Denver, CO. TestAmerica also prepared splits of the methanol extracted samples.

WVDAQ has identified a subset of the MM-0010 sample trains collected during the two sampling events as their priority for ORD's targeted and non-targeted analysis for PFAS compounds. These include samples collected at 3 emission locations within the facility:

- PTFE (T6) area at emission point T6IZCE collected in August 2018 (Run 1)
- PFA (C1) area at emission point C1FSE collected in November 2018 (Run 1)
- FEP (C2) area at emission point C2DTE collected in November 2018 (Run 1)

Priority samples represent a total of 6 MM-0010 sampling trains yielding 24 individual samples. Sampling details are also provided in Table 3.

**Table 3. List of sampling location and events. MM-0010 trains were used in each sampling event at the inlet and outlet of the control device/scrubber. Each MM-0010 train produces 4 individual samples.**

	Chemours Sampling Event	General Description	Secondary Description	Tertiary Descriptor	Number of Samples
ORD Priority Analysis	August 2018	PTFE (T6) Area (emission point T61ZCE)	T61FC Inlet	Run 1	4
			T61ZC Outlet	Run 1	4
	November 2018	PFA (C1) Area (emission point C1FSE)	C1FSC2 Inlet	Run 1	4
			C1FSC3 Outlet	Run 1	4
		FEP (C2) emission point C2DTE	FEPC2 Inlet	Run 1	4
			FEPC2 Outlet	Run 1	4
	Both Sampling events	QA Samples	Trip blanks, reagent blanks, spikes, duplicates, etc.		Up to 26
As Needed		Runs 2 and 3 as listed above	6 MM-0010 trains (at 3 emission points) x 4 samples/train x 2 runs		48

WVDAQ will coordinate with Chemours to have specific sample splits of primary interest sent to the ORD laboratory in Research Triangle Park, NC. TestAmerica will also include split samples of all relevant quality assurance samples collected during the field sampling. These include trip blanks, reagent blanks, spikes, and duplicates.

WVDAQ will obtain extracts from all 3 runs at these two locations representing a total of 72 sample extracts plus quality assurance samples. ORD will prioritize analysis of samples from run 1 (24 sample extracts) as originally requested by WVDAQ (Table 3). In addition, ORD may also process samples from runs 2 and 3 as needed to evaluate emissions estimates.

ORD may also use some of the non-priority samples from runs 2 and 3 to support additional methods development for sampling and analyzing PFAS compounds in air emissions. ORD is experimenting with GC/MS mass spectrometry for analysis of perfluorotelomer alcohol (E-1) that is of specific interest to WVDAQ. ORD is also experimenting with sampling methods for detecting PFAS compounds in air emissions directly. ORD will work with WVDAQ during the course of the study to further evaluate air sampling and analysis methods and may apply additional testing as determined by WVDAQ. This study plan will be amended as needed.



## 2.3 Shipping and Chain of Custody Procedures

Samples will be sent to ORD using the shipping and chain of custody (CoC) procedures described below.

TestAmerica will ship split sample extracts to Dr. Mark Strynar located at Research Triangle Park, NC at the following address.

Attn: Mark Strynar [Strynar.mark@epa.gov](mailto:Strynar.mark@epa.gov)  
US EPA  
109 TW Alexander Dr.  
Chemical Services, Room E-178, Building E Loading Dock  
Research Triangle Park, NC 27709

Each sample will be clearly labeled with a unique sample ID. Samples will be accompanied by a chain of custody (CoC) form(s) that includes, at a minimum, the sample ID and all ancillary information relating to its collection (when, where, and by whom), processing (MM-0010 component), storage, and shipment. Unique sample IDs are defined by the field collectors or WVDAQ and will be clearly labeled. ORD laboratory staff will use these assigned sample IDs when reporting data. All samples shall be shipped according to safety and Department of Transportation (DOT) regulations (i.e., with proper chemical labeling).

The CoC form will record shipping information including shipped by name/date, received by name/date and any special comments (e.g., sample leak). Upon receipt at the laboratory, the sample custodian will check the contents of each shipping container for sample container breakage and will verify that contents match the CoC received. Samples are to be shipped on ice by next day service to be received by ORD on a Tues., Wed., or Thurs. When samples are shipped, an email should be sent to [Strynar.mark@epa.gov](mailto:Strynar.mark@epa.gov) and [Medina-Vera.Myriam@epa.gov](mailto:Medina-Vera.Myriam@epa.gov) providing a heads-up to expect samples. It is recommended that samples be shipped via FedEx who has better delivery times to the RTP facility.

Dr. Strynar or surrogate will sign the chain of custody form and will send an email to POC's at EPA Region 3 and WVDAQ upon receipt of the samples. A copy of the CoC form will be retained by the ORD PI and archived in the EPA/ORD PFAS External Project file upon project completion.

The sample extracts will be stored in a refrigerator/freezer at the RTP laboratory at  $\leq 4^{\circ}\text{C}$ . Holding times are not established for methanol extracts. Accordingly, we do not know the holding time impact on our concentration estimates.

## 2.4 Laboratory Analysis

Extraction of samples was performed by TestAmerica in the laboratory following protocols provided in Appendix A.

Targeted and non-targeted analysis of the extracts will be conducted by ORD PIs on a liquid chromatograph coupled to a tandem mass spectrometer (LC/MS-MS). Laboratory analysis will be led by Dr. Mark Strynar, who is an expert in the area of polyfluoroalkyl substances (PFAS)

including perfluoroalkyl ether carboxylic acids (PFECAs) and has authored numerous papers on the subject.

The project is also supported by Jeff Ryan, who is an expert in emissions sampling and analysis of compounds and particles from source stacks, and vents. Dr. John Offenberg is an expert in tropospheric atmospheric chemistry. These PIs will offer advice on sampling and QA/QC, coordinate sample processing, and assist WVDAQ with emission estimates based on laboratory results.

Sample extracts will be analyzed in the LC/MS under full-scan ( $m/z$  100-1700) conditions. The liquid chromatography instrumentation separates compounds with mixtures based on their spectra. The mass spectrometry instrumentation provides structural identity of the individual components with high molecular specificity and detection sensitivity.

Laboratory analysis will follow the procedures for targeted and non-targeted analysis of PFAS compounds for liquid samples as described in greater detail in ORD's PFAS targeted and non-targeted Quality Assurance Project Plans (QAPPs) listed in Table 4. QAPP documentation includes a description of the analytical process, method SOPs, QA/QC, and laboratory records management.

**Table 4. Supporting Sampling and Analytical and Quality Assurance Documentation**

Organization	Title	Doc ID
EPA/ORD/NERL	Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) in Liquid Samples	D-EMMD-0031917-QP-1-0
EPA/ORD/NERL	Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) in Liquid Samples	D-EMMD-0031918-QP-1-0

The ORD laboratory will receive up to 150 individual samples from runs 1, 2 and 3 collected in the MM-0010 trains during the two sampling events at the Chemours facility, including QA/QC samples. ORD will prioritize analysis of 24 samples from run 1 as specified in Table 3. Targeted analysis and non-targeted suspect screening analysis will be performed on each of the 24 priority samples and the relevant QA/QC samples (Table 5).

**Table 5. Summary of ORD priority analysis of samples to be provided from Chemours facility.**

Media	Targeted PFAS Compounds (Quantification of up to 24, including emerging compounds of concern)	Non-targeted PFAS Compounds Presence of spectrum of PFAS, semiquantitative
Extracts from MM-0010 sampling trains	24	24
QA/QC Samples	All available	All available

**Targeted Analysis.** In targeted analysis, PFAS analytes with known chemical structure are identified by comparison of peak area and retention times (RT) to an authentic standard obtained either from commercial sources or developed by ORD through ongoing research. ORD has developed standards for 24 PFAS compounds, 16 of which are listed in Table 6. These compounds are routinely identified and quantitated during targeted PFAS analysis. This group includes PFOA and HPFO-DA that is of most interest to WVDAQ.

This target or “legacy” analysis will be reported as a concentration and include PFOA and HFPO-DA (GenX) that were previously analyzed by TestAmerica. Results are typically reported in ng/L. High concentrations that may be present in emission extractions may be reported in µg/L and will be clearly labeled in data reports and Excel files.

**Table 6. A list of 16 PFAS compounds quantitated in the ORD lab based on standards.**

Short Name	Chemical Name	Formula	CAS no.	Monoisotopic Mass (g/mol)
GenX	Perfluoro(2-methyl-3-oxahexanoic) acid	C <sub>6</sub> HF <sub>11</sub> O <sub>3</sub>	13252-13-6	329.9750
PFBA	Perfluorobutanoic Acid	C <sub>4</sub> HF <sub>7</sub> O <sub>2</sub>	375-22-4	213.9865
PFPeA	Perfluoropentanoic Acid	C <sub>5</sub> HF <sub>9</sub> O <sub>2</sub>	2706-90-3	263.9833
PFHxA	Perfluorohexanoic Acid	C <sub>6</sub> HF <sub>11</sub> O <sub>2</sub>	307-24-4	313.9801
PFHpA	Perfluoroheptanoic Acid	C <sub>7</sub> HF <sub>13</sub> O <sub>2</sub>	375-85-9	363.9769
PFOA	Perfluorooctanoic Acid	C <sub>8</sub> HF <sub>15</sub> O <sub>2</sub>	335-67-1	413.9737
PFNA	Perfluorononanoic Acid	C <sub>9</sub> HF <sub>17</sub> O <sub>2</sub>	375-95-1	463.9705
PFDA	Perfluorodecanoic Acid	C <sub>10</sub> HF <sub>19</sub> O <sub>2</sub>	335-76-2	513.9673
PFBS	Perfluorobutane Sulfonate	C <sub>4</sub> HF <sub>9</sub> SO <sub>3</sub>	375-73-5	299.9503
PFHxS	Perfluorohexane Sulfonate	C <sub>6</sub> HF <sub>13</sub> SO <sub>3</sub>	355-46-4	398.9366
PFOS	Perfluorooctane Sulfonate	C <sub>8</sub> HF <sub>17</sub> SO <sub>3</sub>	1763-23-1	499.9375
PFUnDA	Perfluoroundecanoic acid	C <sub>11</sub> HF <sub>21</sub> O <sub>2</sub>	2058-94-8	563.9641
PRDoDA	Perfluorododecanoic	C <sub>12</sub> HF <sub>23</sub> O <sub>2</sub>	307-55-1	613.9609
PFTTrDA	Perfluorotridecanoic acid	C <sub>13</sub> HF <sub>25</sub> O <sub>2</sub>	72629-94-8	663.9577
PFPeS	Perfluoropentanesulfonic acid	C <sub>5</sub> HF <sub>11</sub> SO <sub>3</sub>	2706-91-4	349.9471
PFTeDA	Perfluorotetradecanoic acid	C <sub>14</sub> HF <sub>27</sub> O <sub>2</sub>	376-06-7	713.9545

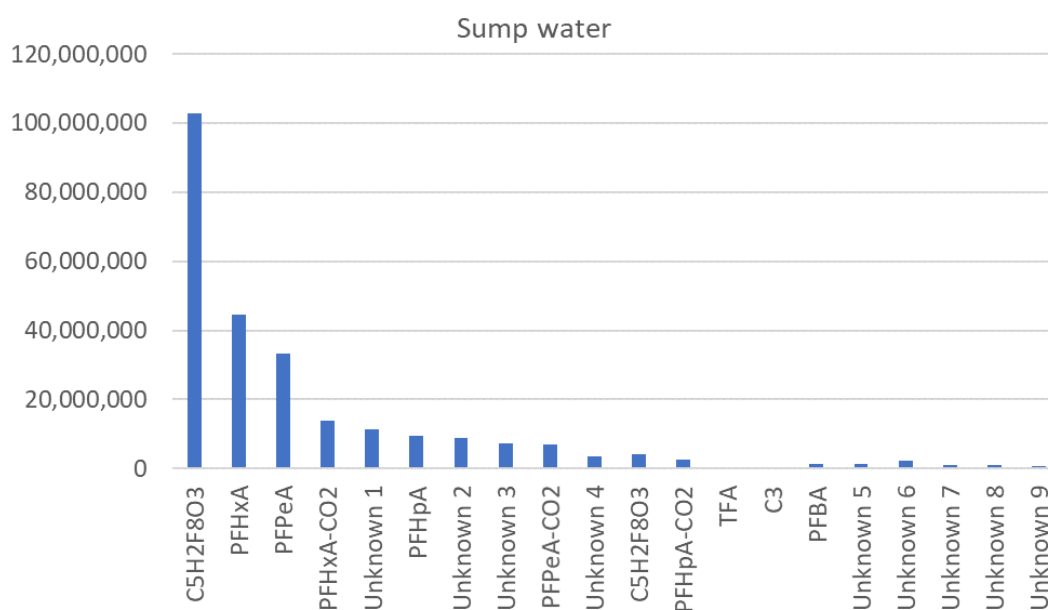
**Non-targeted Analysis.** In non-targeted analysis, detected masses have features such as the m/z values of peaks, retention time (RT), molecular weight, and isotope patterns, but there are no standards available to identify them. The analyst looks for compounds with negative mass defect, characteristics indicative of PFAS, with relatively larger areas. The analyst will attempt to identify them by comparing them to mass spectral libraries and/or in house, putative identifications. ORD may be able to identify the chemical structure of some of the PFAS, but most are of unknown structure and identified by their monoisotopic mass only. ORD scientists generally report a tentatively identified compound cannot be identified, its chromatographic retention times and ‘area under the curve’ are reported and the compound is listed as an unknown. The amount present is reported as relative abundance.

An example NTA analysis result for a similar sampling of stack control devices where the

relative abundance of known and unknown PFAS is provided in Figure 1. Unlike Figure 1, ORD may be able to provide a semiquantitative estimate of PFAS compounds identified by NTA based on comparison to the closest relative compound identified in the targeted analysis.

Note that ORD is not able to evaluate the concentrations of fluoroether (E-1) as originally requested by WVDAQ using these techniques. However, ORD is also experimenting with GC/MS mass spectrometry methods and may be able to detect fluoroether E-1 in XAD resins with this instrumentation and will report results for E-1 if successful. It will not be possible to report volatile PFAS emissions quantitatively.

**Figure 1. Example non-targeted analysis result. Note that analytes are expressed in relative abundance (left vertical axis) and that analytes consist of some with known structures and some that are unknown.**



## 2.5 Quality Assurance

ORD will evaluate on QA/QC sampling performance to the extent that QC samples are provided by TestAmerica. Results of the QA assessment will influence confidence levels in any comparisons of results between laboratories that will be performed in this study. The opportunity for quality control measures varies between targeted and non-targeted analyses.

### 2.5.1 Targeted Analysis

ORD analysts conduct a number of QC tests of for precision, accuracy, and method sensitivity while processing samples, including laboratory calibration curves, and reporting of levels of detection and quantitation for targeted analysis. ORD's overall Quality Assurance (QA) objective is to provide data that can be shown to be of high quality. These include evaluation Quality Control (QC) and Method Evaluation samples collected during laboratory testing and during field sampling (e.g. field spikes, field blanks, transport blanks, etc.). Our ability to

quantify and evaluate QA/QC performance of samples received from TestAmerica will depend on the availability of QC samples collected during stack testing by the Chemours contractors. Splits of all QA/QC samples should be included with the samples obtained from TestAmerica.

All laboratory analysis results provided to WVDAQ will be flagged as appropriate if quality assurance objectives are not met.

Laboratory Calibration. The calibration of the LC-MS/MS response for individual compounds is based on the calibration curve solutions that are analyzed with each sample batch. In general, a 7-point calibration curve that spans the linear instrument detection range is analyzed at the beginning and end of each batch of samples analyzed. The correlation coefficient for the calibration should be  $> 0.98$  for the calibration to be accepted.

Method sensitivity: The lower limit of quantitation (LLOQ) is defined as the lowest point of calibration curve at which level the signal-to-noise ratio was at least 10:1 with precision of 15% (CV) and accuracy of 100%  $\pm$  30%.

The limit of quantitation (LOQ) for targeted analysis is the lowest point on the calibration curve (e.g., 10.0 ng/L). However, lower LOQs are achievable with this method through modification of the concentration step which will be documented if used. The verified calibration range of the method used is 10-1000 ng/L.

Precision: Precision is reported as the relative percent difference for duplicate samples. This applies to field duplicates and laboratory duplicates. The precision goal, as measured as the % difference between duplicate samples is  $< 30\%$ .

$$\text{Relative \% Difference} = [(\text{conc.1} - \text{conc. 2}) / (\text{mean of conc.1 and 2})] \times 100\%$$

Accuracy: Accuracy is reported as percent difference between the concentration of a sample prepared by spiking a target compound into a blank matrix and concentration being determined using a standard curve which is compared to the theoretical calculated concentration recorded in the laboratory notebook. Percent accuracy of any spiked trip QA samples should be within  $\pm 30\%$  of the theoretical concentrations.

$$\text{Accuracy} = (\text{spike level determined by standard curve} / \text{theoretical spike concentration}) \times 100\%$$

Finally, blank samples (trip blanks, method blanks and solvent blanks) should be free of analytes to demonstrate control of field or laboratory contamination that may exist.

#### 2.5.2 Non-targeted Analysis

The estimation of additional PFAS that are not able to be quantitated due to lack of commercially available standards are to be semi-quantitatively estimated by best effort using available information. Quality assurance is limited to repeatability of sample processing. For extract samples, replicate analysis precision should be within  $\pm 50\%$ .

## 2.6 Data Reporting

ORD will provide results of PFAS concentration in the liquid extract in units of mass per unit volume, e.g. nanograms per liter to WVDAQ batched by analysis type (targeted, NTA) as soon as they have been quality assured and cleared at EPA. Non-targeted analysis requires considerably greater processing time. The timing and content of reports can be negotiated with WVDAQ as the project proceeds.

ORD will provide laboratory results to WVDAQ and Region 3 via a formal data report that includes a transmittal letter from the Lab Director and attached data report. The results and report will undergo a rigorous review process including internal scientific and QA review. The data report will address the following topics:

- Samples identified by WVDAQ or TestAmerica naming convention in the sampling plan and bottle labels listed in CoC's;
- Brief description of how samples were collected, shipped, and processed including laboratory methods,
- A table of sample IDs, PFAS compounds and their concentrations or relative abundance and appropriate flags;
- A brief summary of Quality Control results.
- A brief summary of results.

The data report will undergo an elevated clearance process within EPA including review by Region 3 and program offices.

EPA/ORD communication of data report findings is limited to Region 3 and WVDAQ. ORD will consult with WVDAQ about any use of the data including internal or external sharing of findings.

ORD will provide a summary report or memorandum to WVDAQ and Region 3 when all analyses and tasks in this study plan are completed. WVDAQ and ORD will determine the content of the final report.

## 2.7 Additional Analyses

Comparison of PFOA and GenX. An objective of WVDAQ is to compare laboratory analytical results for PFOA and HPFO generated by ORD with earlier results provided by TestAmerica. WVDAQ will be responsible for making laboratory comparisons. ORD will advise WVDAQ on the accuracy and precision that can be expected from ORD's analyses and any limitations due to lack of necessary metadata. Possible explanations for observed differences in concentration values between ORD and Chemours/contractors include differences in laboratory methods, processing, and holding times.

Emissions Estimates. An additional objective of WVDAQ is to utilize PFAS concentrations from laboratory testing to estimate air emissions and control device effectiveness. The ability to do this will depend on the availability of critical testing information, such as total liquid volumes and gaseous sample volumes obtained during the stack testing events.

Critical stack testing information will be required to estimate sampling efficiency and so on. WVDAQ will obtain the necessary information from Chemours to perform those analyses by February 28, 2019. Based on the analytical results from the priority samples, ORDs PI Jeff Ryan will work with WVDAQ to estimate emissions to the air from the facility. An emissions assessment plan will be developed by WVDAQ and ORD and will be appended to this study plan by March 26, 2019.

## 2.8 Expected products

- 1) Full quantification of concentrations of HFPO-DA (GenX), PFOA, and 22 additional PFAS analytes with standards in liquid extract samples to be provided in a data report.
- 2) Identification and semi-quantification of additional PFAS concentrations in liquid extracts that are amenable to LC/MS analysis using suspect screening and non-targeted methods to be provided in a data report.
- 3) Estimates of PFAS air emissions and control technology efficiency, dependent on the availability of critical information collected during stack testing. Product to be determined.

## 2.9 Schedule

The projected timeline for deliverables is provided in Table 7.

**Table 7. Project timeline ADD IN PHASE 1 and PHASE 2**

Activity/Task	Calendar Year 2018	Calendar Year 2019		
	Q4	Q1	Q2	Q3
Air Field Sample Collection	X			
Develop and Finalize Study Plan		X		
Send sample extracts to ORD (Feb 2019)		X		
Targeted laboratory analysis and reporting of priority samples			X	
Non-targeted data analysis and reporting of priority samples				X
Develop and finalize emission estimation plan			X	

### **3 Communications Plan**

EPA's Region 3 point of contact (POC) will coordinate communications between WVDAQ and ORD and convene meetings on an as-needed basis.

EPA/ORD will provide informal updates to WV DAQ and Region 3. Any discussion of findings in this context are considered preliminary and deliberative and not to be shared or released.

ORD's goal is to provide WVDAQ with data that is timely, of high-quality, and relevant to their regulatory actions. WVDAQ assumes responsibility for communications of findings and any associated risk to the public, impacted communities, water utilities, or industry.

A desk statement summarizing report findings will be prepared by EPA/ORD with review/input from the relevant Region and Program Offices prior to transmitting any data or reports. These desk statements are used by EPA communications should they receive any requests for information.

The data generated in this project may also be used by ORD for scientific presentations and publications. Before any data are made public by ORD, ORD will provide advance notification and consult with WVDAQ and Region 3 POC.

### **4 Records Management**

Mark Strynar (RTP) will maintain all laboratory analysis related documentation for this project including sample preparation records, and LC-MS/MS analysis logs. and the laboratory records describing the preparation and deployment of field quality control (QC) samples.

Kate Sullivan will maintain project file documentation together with all associated communication, reporting of data or findings, field sample tracking forms, and QA/QC documentation. The project file will contain the records of QA issues, amendments to plans and SOPs, audit reports, and corrective action reports.

All records will be maintained as per EPA specifications.



## **Appendix A—Stack Testing Protocols**

## **4. SAMPLING AND ANALYTICAL METHODS**

### **4.1 STACK GAS SAMPLING PROCEDURES**

The purpose of this section is to describe the stack gas emissions sampling trains and to provide detail of the stack sampling and analytical procedures utilized during the emissions test program.

#### **4.1.1 Pre-Test Determinations**

Preliminary test data will be obtained at each test location. Stack geometry measurements will be measured and recorded, and traverse point distances verified. A preliminary velocity traverse will be performed utilizing a calibrated "S" type pitot tube and an inclined manometer to determine velocity profiles. Flue gas temperatures will be observed with a calibrated direct readout panel meter equipped with a chromel-alumel thermocouple. Preliminary water vapor content will be measured by performance of an EPA Method 4 moisture test or by wet bulb/dry bulb temperature measurements.

A check for the presence or absence of cyclonic flow will be conducted at each test location.

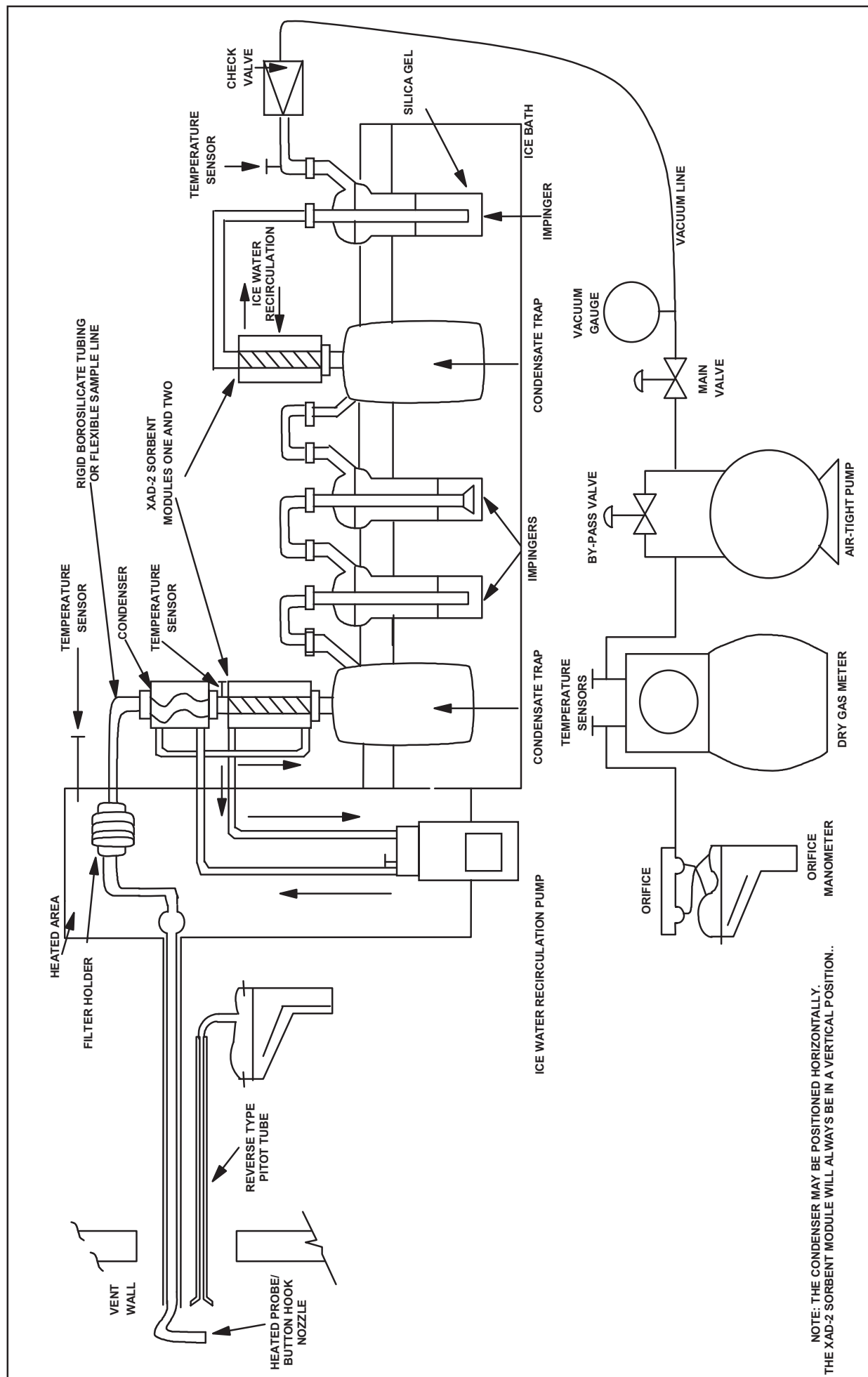
Preliminary test data will be used for nozzle sizing and sampling rate determinations for isokinetic sampling procedures.

Calibration of probe nozzles, pitot tubes, metering systems, and temperature measurement devices will be as specified in Section 5 of EPA Method 5 test procedures.

### **4.2 STACK PARAMETERS**

#### **4.2.1 EPA Method 0010**

The sampling train utilized to perform the HFPO Dimer Acid sampling will be an EPA Method 0010 train (see Figure 4-1). The Method 0010 consists of a borosilicate or stainless steel nozzle that will be attached directly to a heated borosilicate probe. In order to minimize possible thermal degradation of the HFPO Dimer Acid, the probe and particulate filter will be heated above stack temperature to minimize water vapor condensation before the filter. The probe will be connected directly to a heated borosilicate filter holder containing a solvent extracted glass fiber filter.



**FIGURE 4-1**  
**EPA METHOD 0010 SAMPLING TRAIN**

A section of borosilicate glass or flexible polyethylene tubing will connect the filter holder exit to a Graham (spiral) type ice water-cooled condenser, an icewater-jacketed sorbent module containing approximately 40 grams of XAD-2 resin. The XAD-2 resin tube is equipped with an inlet temperature sensor. The XAD-2 resin trap will be followed by a condensate knockout impinger and a series of two impingers containing 100-ml of high purity distilled water. The train will also include a second XAD-2 resin trap behind the impinger section to evaluate possible sampling train breakthrough. Each XAD-2 resin trap will be connected to a 1-L condensate knockout trap. The final impinger will contain 300 grams of dry pre-weighed silica gel. All impingers and the condensate traps will be maintained in an ice bath. Ice water will be continuously circulated in the condenser and both XAD-2 modules to maintain method required temperature. A control console with a leakless vacuum pump, a calibrated orifice, and dual inclined manometers will be connected to the final impinger via an umbilical cord to complete the sample train.

During sampling, gas stream velocities will be measured by attaching a calibrated "S"-type pitot tube into the gas stream adjacent to the sampling nozzle. The velocity pressure differential will be observed immediately after positioning the nozzle at each traverse point, and the sampling rate adjusted to maintain isokineticity  $\pm 10$ . Flue gas temperature will be monitored at each point with a calibrated panel meter and thermocouple. Isokinetic test data will be recorded at each traverse point during all test periods, as appropriate. Leak checks will be performed on the sampling apparatus according to reference method instructions, prior to and following each run, component change (if required) or during midpoint port changes.

#### **4.2.2 EPA Method 0010 Sample Recovery**

At the conclusion of each test, the sampling train will be dismantled, the openings sealed, and the components transported to the field laboratory trailer for recovery.

A consistent procedure will be employed for sample recovery:

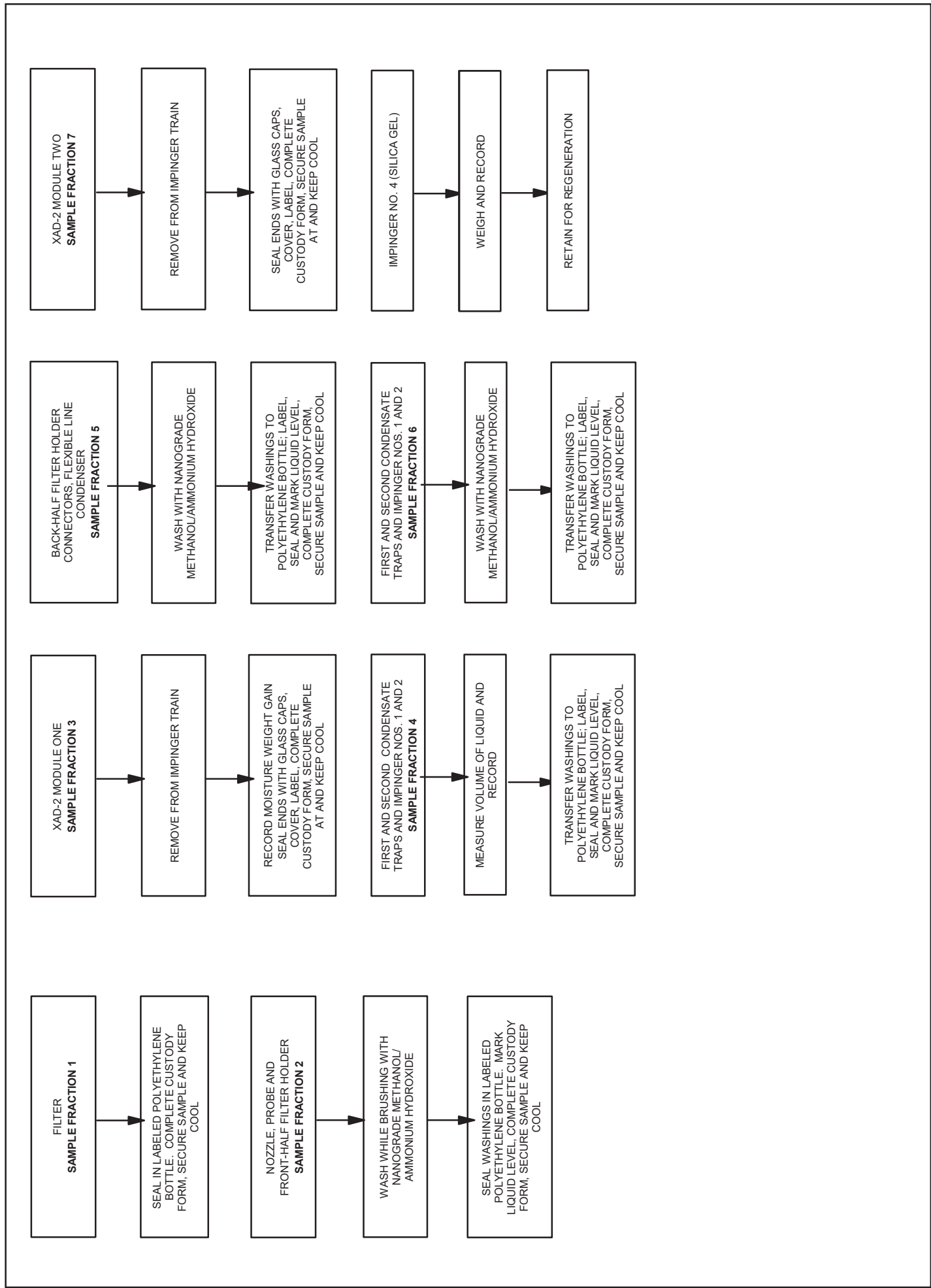
1. The two XAD-2 covered (to minimize light degradation) sorbent modules (1 and 2) will be sealed and labeled.

2. The glass fiber filter(s) will be removed from the holder with tweezers and placed in a polyethylene container along with any loose particulate and filter fragments.
3. The particulate adhering to the internal surfaces of the nozzle, probe and front half of the filter holder will be rinsed with a solution of methanol and ammonium hydroxide into a polyethylene container while brushing a minimum of three times until no visible particulate remains. Particulate adhering to the brush will be rinsed with methanol/ammonium hydroxide into the same container. The container will be sealed.
4. The volume of liquid collected in the first condensate trap will be measured, the value recorded, and the contents poured into a polyethylene container.
5. All train components between the filter exit and the first condensate trap will be rinsed with methanol/ammonium hydroxide. The solvent rinse will be placed in a separate polyethylene container and sealed.
6. The volume of liquid in the impingers one, two, and second condensate trap will be measured, the values recorded, and sample will be placed in the same container as step 4 above and sealed.
7. The two impingers, condensate trap, and connectors will be rinsed with methanol/ammonium hydroxide. The solvent sample will be placed in a separate polyethylene container and sealed.
8. The silica gel in the final impinger will be weighed and the weight gain value recorded.
9. Site (reagent) blank samples of the methanol/ammonium hydroxide, XAD resin, filter and distilled water will be retained for analysis.

Each container will be labeled to clearly identify its contents. The height of the fluid level will be marked on the container of each liquid sample to provide a reference point for a leakage check during transport. All samples will be maintained cool.

During each test campaign, a M-0010 blank train will be setup near the test location, leak checked (twice) and recovered along with the respective sample train. Following sample recovery, all samples will be transported to the TestAmerica Inc. for sample extraction and analysis.

See Figure 4-2 for a schematic of the M-0010 sample recovery process.



**FIGURE 4-2**  
**HFPO DIMER ACID SAMPLE RECOVERY PROCEDURES FOR METHOD 0010**

### 4.2.3 EPA Method 0010 – Sample Analysis

Method 0010 sampling trains will result in four separate analytical fractions for HFPO Dimer Acid analysis according to SW-846 Method 3542:

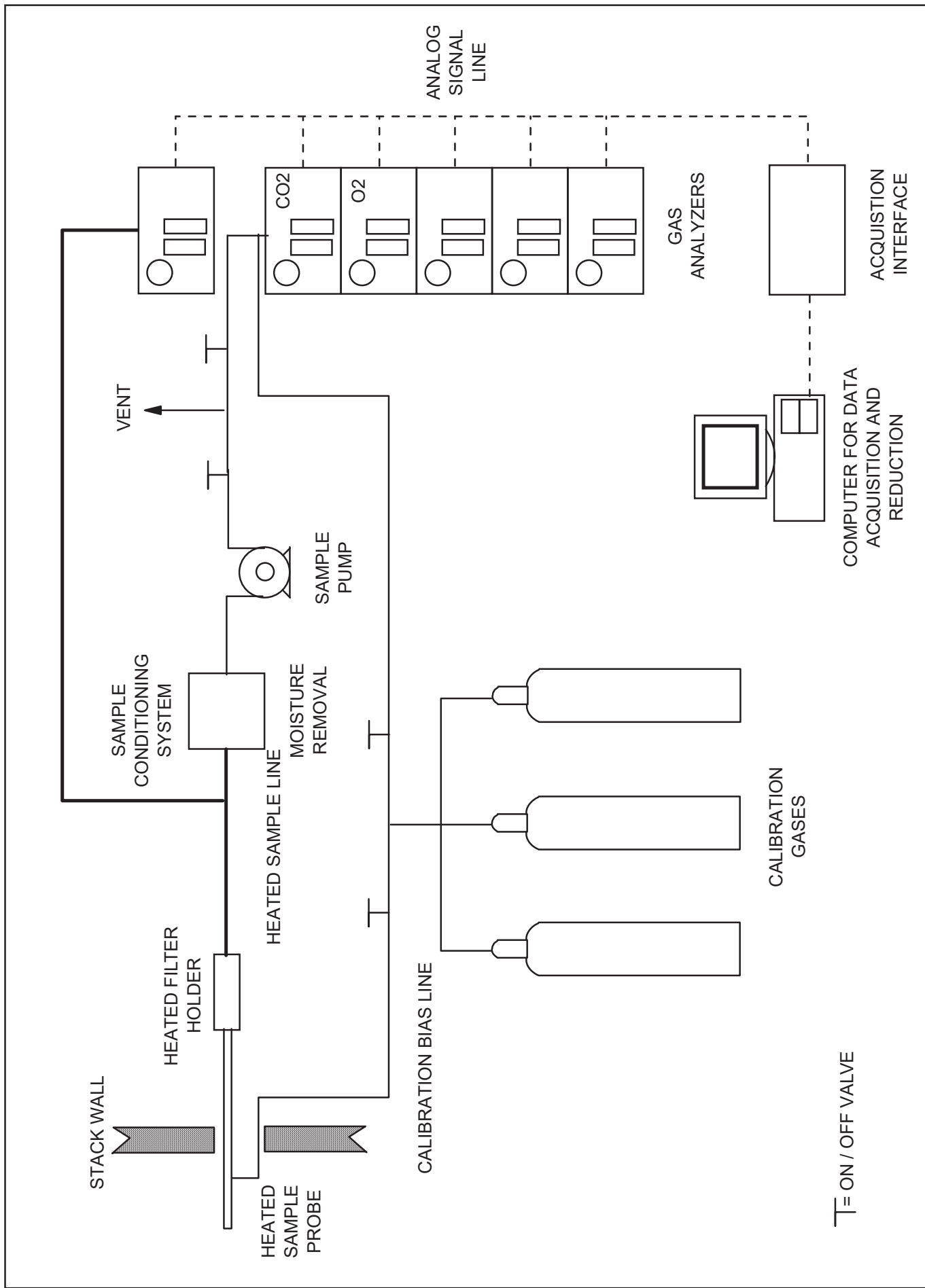
- Front-Half Composite—comprised of the Particulate Filter, and the probe, nozzle, and front-half of the filter holder solvent rinses,
- Back-half Composite—comprised of the first XAD-2 resin material and the back-half of the filter holder with connecting glassware solvent rinses,
- Condensate Composite—comprised of the aqueous condensates and the contents of Impingers #1 and 2 with solvent rinses,
- Breakthrough XAD-2 Resin Tube—comprised of the resin tube behind the series of impingers.

The second XAD-2 resin material will be analyzed separately to evaluate any possible sampling train HFPO-DA breakthrough.

The Front and Back-half composites and the second XAD-2 resin material will be placed in polypropylene wide-mouth bottles and tumbled with methanol containing 5% NH<sub>4</sub>OH for 18 hours. Portions of the extracts will be processed analytically for the HFPO dimer acid by Liquid Chromatography and dual mass spectroscopy (HPLC/MS/MS). The Condensate composite will be concentrated onto a solid phase extraction (SPE) cartridge followed by desorption from the cartridge using methanol. Portions of those extracts will also be processed analytically by HPLC/MS/MS.

Samples will be spiked with isotope dilution internal standard (IDA) at the commencement of their preparation to provide accurate assessments of the analytical recoveries. Final data will be corrected for IDA standard recoveries.

Test America has developed detailed procedures for the sample extraction and analysis for HFPO Dimer Acid. These procedures are incorporated into this test protocol in Appendix A.



**FIGURE 4-3**  
**WESTON SAMPLING SYSTEM**



### 4.3 GAS COMPOSITION

A mobile laboratory equipped with instrumental analyzers will be used to measure carbon dioxide (CO<sub>2</sub>), and oxygen (O<sub>2</sub>) concentrations. A diagram of the WESTON sampling system is presented in Figure 4-3.

A heated stainless steel probe will be used to collect a sample at the approximate centroid of each stack. At the end of the probe, a tee will permit the introduction of calibration gas. The sample will be drawn through a heated Teflon® sample line to the sample conditioner. The output from the sampling system will be recorded electronically, and one-minute averages will be recorded and displayed on a data logger. As an option, the sample may be collected at the exhaust of the Method 0010 sampling system.

Each analyzer will be set up and calibrated internally by introduction of calibration gas standards directly to the analyzer from a calibration manifold. The calibration manifold is designed with an atmospheric vent to release excess calibration gas and maintains the calibration at ambient pressure. The direct calibration sequence will consist of alternate injections of zero and mid-range gases with appropriate adjustments until the desired responses are obtained. The high range standards will then be introduced in sequence without further adjustment.

The sample line integrity will be verified by performing a bias test before and after each test period. The sampling system bias test consists of introducing the zero gas and one up range calibration standard in excess to the valve at the probe end when the system is sampling normally. The excess calibration gas flows out through the probe to maintain ambient sampling system pressure. Calibration gas supply is regulated to maintain constant sampling rate and pressure. Instrument bias check response will be compared to internal calibration responses to insure sample line integrity and to calculate a bias correction factor after each run using the ratio of the measured concentration of the bias gas certified by the calibration gas supplier.

The oxygen and carbon dioxide content of each stack gas will be measured according to EPA Method 3A procedures which incorporate the latest updates of EPA Method 7E. A Servomex Model 4900 analyzer (or equivalent) will be used to measure oxygen content. A Servomex Model 4900 analyzer (or equivalent) will be used to measure carbon dioxide content of the stack gas. Both analyzers will be calibrated with EPA Protocol gases prior to the start of the test program and performance will be verified by sample bias checks before and after each test run.

## 5. TEST PROCEDURES

Each test will be a minimum of 180 minutes in duration and sufficient to collect  $\geq 3\text{m}^3$  (105.9 ft<sup>3</sup>) of sample volume. A total of three test runs per location will be performed.

Note that if preliminary analytical results require significant sample dilution to bring the HFPO Dimer Acid concentration within instrument calibration, the sample time and sample volume may be reduced. This will require the approval of the North Carolina Department of Environmental Quality (NC DEQ).

## 6. TEST REPORT FORMAT

A written final report will be prepared for NC DEQ. The report will be submitted within 90 days of test completion. The test report will include:

1. A summary section which will contain a concise description of the Emissions Test program including reasons for testing, number and types of tests, technical approach, etc. A summary table showing key test data and results.
2. A description of the test locations and sampling equipment used for the tests.
3. A description or reference of sampling and analytical procedures.
4. Test data and results summary tables. Emissions will be reported on a concentration basis (lb/dscf, ug/m<sup>3</sup>) and mass basis (lb/hr, gm/sec).
5. A discussion section will include comments concerning any unusual process conditions or difficulties experienced with testing or analytical procedures.
6. Appendices containing:
  - Process operations data (process operating and control data to be monitored and supplied by Chemours).
  - Raw and reduced test data.
  - Laboratory analytical report.
  - Sample calculations.
  - Equipment calibration records.
  - List of project participants.

## **7. QUALITY ASSURANCE AND CALIBRATIONS**

The following procedures will be followed to insure that the emissions data collected during this test program are of high quality.

### **7.1 VELOCITY/VOLUMETRIC FLOW RATE QC PROCEDURES**

Volumetric flow rates will be determined using EPA Methods 1 and 2. The following QC steps will be followed during these tests:

- The pitot tube will be visually inspected before sampling.
- Both legs of the pitot tube will be leak-checked before sampling.
- The manometer oil will be leveled and zeroed before each run and periodically checked.
- Cyclonic flow checks using an S-type pitot tube will be performed once per source during testing.
- Pitot tube coefficients will be determined based on physical measurement techniques as delineated in Method 2.

### **7.2 MOISTURE CONTENT AND SAMPLE VOLUME QC PROCEDURES**

Gas stream moisture will be determined by EPA Method 4 as part of the M-0010 isokinetic stack tests. The following QC procedures will be followed in determining the volume of moisture collected:

- The amount of moisture collected will be determined either volumetrically or gravimetrically.
- The balance will be calibrated daily.
- The balance zero will be checked and re-zeroed if necessary before each weighing.
- The balance will be leveled and placed in a clean, motionless environment for weighings.
- The indicating silica gel will be fresh for each run and periodically inspected and replaced during runs if needed.

The QC procedures that are followed in regard to accurate sample gas volume determination will be:

- The dry gas meter will be fully calibrated annually using an EPA-approved intermediate standard device.
- Pre-test, port-change, and post-test leak-checks will be completed (must be less than 0.02 cubic feet per minute (cfm) or 4% of the average sample rate).
- The gas meter will be read to the thousandth of a cubic foot for all initial and final readings.
- Readings of the dry gas meter, meter orifice pressure (Delta H) and meter temperatures will be taken at every sampling point.
- Accurate barometric pressures will be recorded at least once per day.
- Pre- and post-test program dry gas meter checks will be completed to verify the accuracy of the meter calibration constant (Y).

### **7.3 METHOD 0010 SAMPLING QC PROCEDURES**

The specific sampling QC procedures which will ensure representative collection of Method 0010 data are as follows:

- Pre-clean sample and recovery glassware as described in Method 0010.
- The XAD-2 resin material used to collect these samples has been lot tested for HFPO-DA background. Media checks and various blanks will provide ongoing indicators of resin continued cleanliness and its appropriate storage condition.
- Only nanograde or equivalent solvents and reagents will be used for test train preparation and recovery. High purity distilled water will be used.
- The sample rate must be within 10% of the true isokinetic (100%) rate.
- All sampling nozzles will be manufactured and calibrated according to EPA standards.
- Maintain the XAD-2 resin gas stream inlet and silica gel exit gas stream temperature at or below 68 °F during testing.
- Complete recovery procedures in a clean environment.

- Maintain solvent, XAD and filter samples cool following collection and prior to analysis.
- All calculations will be double-checked for accuracy and completeness.
- All manual test apparatus will be leak checked before and after each test run. Each leak check will be recorded on a field sampling data sheet.

## 7.4 INSTRUMENTAL ANALYZER QC SAMPLING PROCEDURES

The following QC procedures will be applied to ensure collection of representative test data.

- The gas composition sampling systems (probe to sample conditioner) will be leak-checked prior to the testing.
- All analyzers will be calibrated prior to testing to ensure precise and accurate data. Protocol standards will be used to calibrate each of the analyzers. Each analyzer will be calibrated at three to four points (zero, mid, and high range) depending on reference method requirements. Nitrogen will be used to set the instrument zero. The calibration standards will be approximately 40-60 and 100% span for CO<sub>2</sub> and O<sub>2</sub>.
- Prior to formal testing, a stratification check will be performed on each stack. Per Section 8.1.2 of EPA Method 7E, a three point CO<sub>2</sub> or O<sub>2</sub> stratification check passing through the centroidal area of the stack will be performed. The three points (16.7, 50 and 83.3) percent of the stack diameter will each be sampled a minimum of two times the system response. If the CO<sub>2</sub> or O<sub>2</sub> concentration at each point in comparison to the mean difference is no more than  $\pm 5.0$  percent, then all sampling will be performed at a single point at the stack midpoint. If the difference is between 5 percent but not greater than 10 percent, a three point traverse per run will be performed. A difference of greater than 10 percent in concentration will result in performing a twelve point traverse with points calculated per EPA Method 1.
- Pre- and post-test calibration bias tests will be performed for each test run. The bias check will be performed with the calibration standard that is closest to the observed concentration in the sample gas. The average pre/post-test bias drift will not exceed 3 % of full scale.
- A permanent data record of analyzer responses will be recorded using computer software.
- If preliminary measurements of O<sub>2</sub> and CO<sub>2</sub> indicate that the stack gas concentrations are equivalent to ambient air (20.9% O<sub>2</sub>, 0% CO<sub>2</sub>), then further O<sub>2</sub> and CO<sub>2</sub> monitoring may not be required.

## **7.5 DECONTAMINATION PROCEDURES**

Stack gas sampling equipment will be pre-cleaned following standard source test method procedures. All stack gas sampling equipment will be cleaned on-site as part of individual sample recovery procedures.

Sample containers are purchased from a vendor. The vendor provides a certificate indicating that each lot of bottles is free of contaminants.

All personnel associated with sample collection will use designated personal protective equipment (PPE). Personnel will follow standard PPE decontamination procedures for each level of PPE required.

Personnel have received the proper hazardous materials training specified in 29 CFR 1910.

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**APPENDIX A**  
**TEST AMERICA PROCEDURES FOR SAMPLE EXTRACTION AND**  
**ANALYSIS OF HFPO DIMER ACID**

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## TestAmerica HFPO-DA Method 0010 Sampling Train Fraction Preparation and Analysis Summary

The Method 0010 Sampling train fractions are transported from the Chemours Plant site in Fayetteville, NC to the TestAmerica Laboratory in Knoxville, TN for processing. The fractions are collected and recovered from the sampling train according to SW-846 additional guidelines found in Method 3542 for the breakdown of Method 0010 components. The train fraction designations are as follows:

- Front-Half Composite—consisting of a particulate filter, and a probe, nozzle and front portion of the filter holder bell housing glassware solvent rinses,
- Back-Half Composite—consisting of an XAD-2 resin module, and the back portion of the filter holder bell housing with connecting glassware solvent rinses,
- Condensate and Impinger Contents—consisting of the D.I. Water content used to initially charge the impingers and Condensate collected during the sampling run.
- Breakthrough XAD-2 Resin Tube—consisting of a standard XAD-2 module placed behind the Condensate Impingers as a final quality assurance indicator of the lack of breakthrough of the HFPO-DA through the sampling train.

In the laboratory, the Front-Half sample fraction components are placed in to an HDPE bottle and spiked with  $^{13}\text{C}_3$ -HFPO isotope dilution internal standard (IDA). This composite is extracted with basic methanol for 18 hours at room temperature followed by acidification using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA. Instrumental analysis for these extracts is conducted in the TestAmerica Denver Laboratory.

The Back-Half sample fraction components, including the approximately 40 grams of XAD-2 resin material, are transferred to an HDPE bottle and spiked with the IDA internal standard. This Back-Half Composite is extracted at room temperature using two (2) successive 18 hour periods and separate portions of basic methanol. The XAD-2 resin material is removed, and the extraction fluid is acidified using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA in the TestAmerica Denver Laboratory.

The Condensate Composite fraction of the sampling train is measured to record the total volume in the composite followed by preparation by concentration on a solid phase extractor (SPE). The SPE cartridge is treated with water/methanol mixture to release the HFPO-DA. The extract is run for the HFPO-DA using Method 8321A.

The Breakthrough XAD-2 Resin Tube fraction is prepared and analyzed by the same process as that used for the Back-half sampling train fraction.

Due to the sensitivity of the LCMS methodology, concentrations levels collected on Method 0010 sampling trains of HFPO-DA may require significant dilutions in order to report analytical data that is “hard quantified” within the calibration range of the process. The diluted samples avoid “E” (estimated) values for the results of the HFPO-DA.

## **4. SAMPLING AND ANALYTICAL METHODS**

### **4.1 STACK GAS SAMPLING PROCEDURES**

The purpose of this section is to describe the stack gas emissions sampling trains and to provide detail of the stack sampling and analytical procedures utilized during the emissions test program.

#### **4.1.1 Pre-Test Determinations**

Preliminary test data will be obtained at each test location. Stack geometry measurements will be measured and recorded, and traverse point distances verified. A preliminary velocity traverse will be performed utilizing a calibrated "S" type pitot tube and an inclined manometer to determine velocity profiles. Flue gas temperatures will be observed with a calibrated direct readout panel meter equipped with a chromel-alumel thermocouple. Preliminary water vapor content will be measured by performance of an EPA Method 4 moisture test or by wet bulb/dry bulb temperature measurements.

A check for the presence or absence of cyclonic flow will be conducted at each test location.

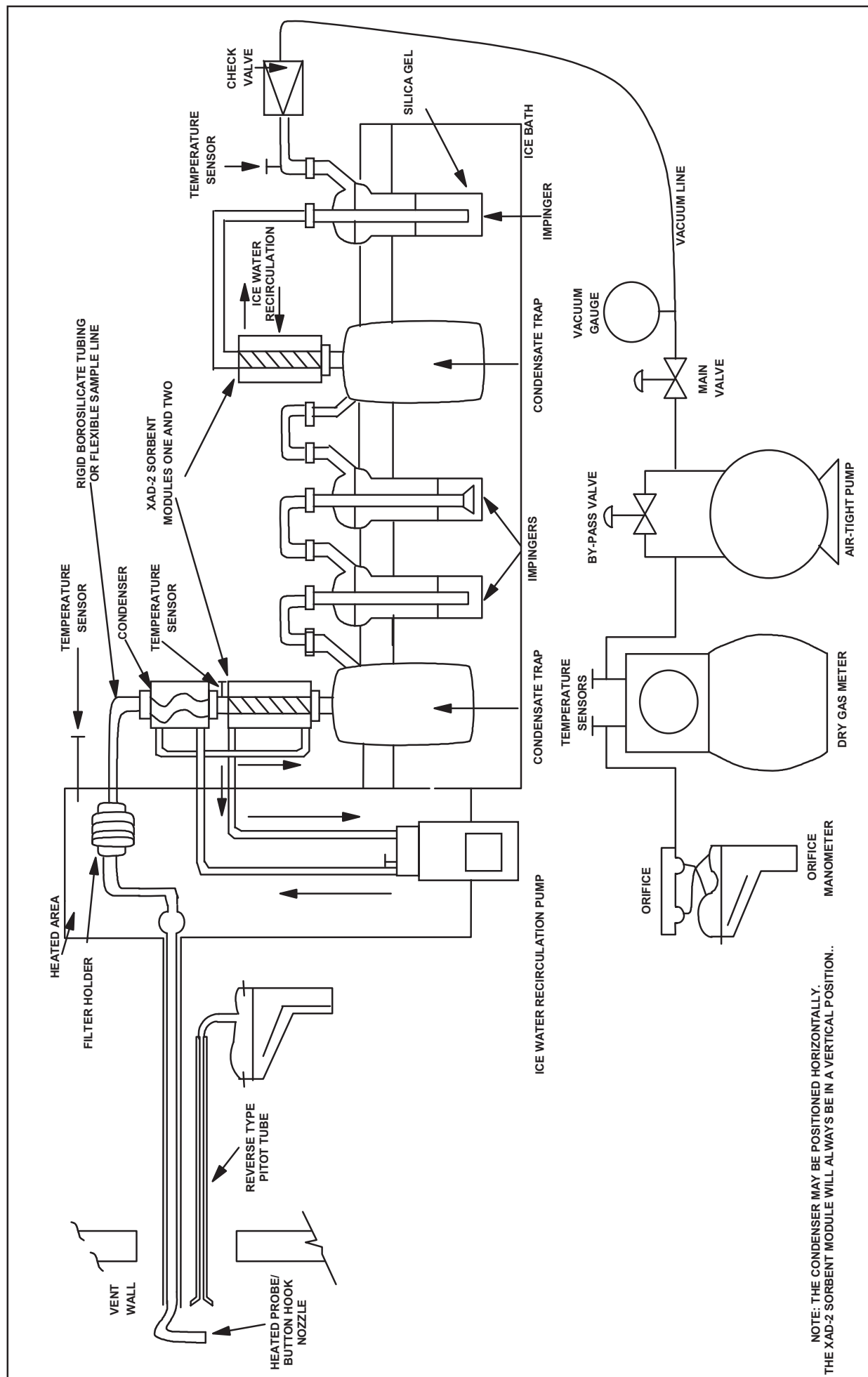
Preliminary test data will be used for nozzle sizing and sampling rate determinations for isokinetic sampling procedures.

Calibration of probe nozzles, pitot tubes, metering systems, and temperature measurement devices will be as specified in Section 5 of EPA Method 5 test procedures.

### **4.2 STACK PARAMETERS**

#### **4.2.1 EPA Method 0010**

The sampling train utilized to perform the HFPO Dimer Acid sampling will be an EPA Method 0010 train (see Figure 4-1). The Method 0010 consists of a borosilicate or stainless steel nozzle that will be attached directly to a heated borosilicate probe. In order to minimize possible thermal degradation of the HFPO Dimer Acid, the probe and particulate filter will be heated above stack temperature to minimize water vapor condensation before the filter. The probe will be connected directly to a heated borosilicate filter holder containing a solvent extracted glass fiber filter.



**FIGURE 4-1**  
**EPA METHOD 0010 SAMPLING TRAIN**

A section of borosilicate glass or flexible polyethylene tubing will connect the filter holder exit to a Graham (spiral) type ice water-cooled condenser, an icewater-jacketed sorbent module containing approximately 40 grams of XAD-2 resin. The XAD-2 resin tube is equipped with an inlet temperature sensor. The XAD-2 resin trap will be followed by a condensate knockout impinger and a series of two impingers containing 100-ml of high purity distilled water. The train will also include a second XAD-2 resin trap behind the impinger section to evaluate possible sampling train breakthrough. Each XAD-2 resin trap will be connected to a 1-L condensate knockout trap. The final impinger will contain 300 grams of dry pre-weighed silica gel. All impingers and the condensate traps will be maintained in an ice bath. Ice water will be continuously circulated in the condenser and both XAD-2 modules to maintain method required temperature. A control console with a leakless vacuum pump, a calibrated orifice, and dual inclined manometers will be connected to the final impinger via an umbilical cord to complete the sample train.

During sampling, gas stream velocities will be measured by attaching a calibrated "S"-type pitot tube into the gas stream adjacent to the sampling nozzle. The velocity pressure differential will be observed immediately after positioning the nozzle at each traverse point, and the sampling rate adjusted to maintain isokineticity  $\pm 10$ . Flue gas temperature will be monitored at each point with a calibrated panel meter and thermocouple. Isokinetic test data will be recorded at each traverse point during all test periods, as appropriate. Leak checks will be performed on the sampling apparatus according to reference method instructions, prior to and following each run, component change (if required) or during midpoint port changes.

#### **4.2.2 EPA Method 0010 Sample Recovery**

At the conclusion of each test, the sampling train will be dismantled, the openings sealed, and the components transported to the field laboratory trailer for recovery.

A consistent procedure will be employed for sample recovery:

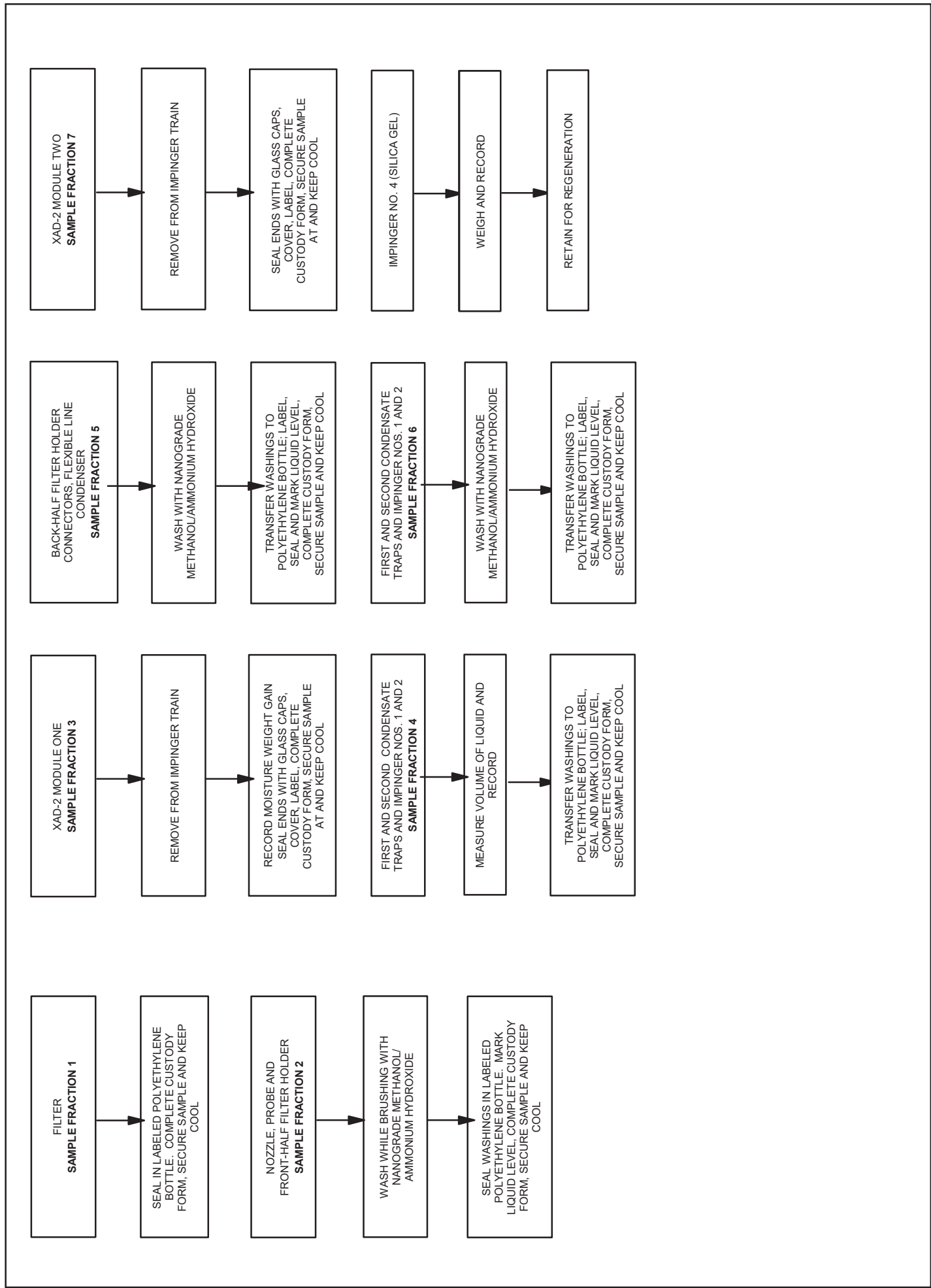
1. The two XAD-2 covered (to minimize light degradation) sorbent modules (1 and 2) will be sealed and labeled.

2. The glass fiber filter(s) will be removed from the holder with tweezers and placed in a polyethylene container along with any loose particulate and filter fragments.
3. The particulate adhering to the internal surfaces of the nozzle, probe and front half of the filter holder will be rinsed with a solution of methanol and ammonium hydroxide into a polyethylene container while brushing a minimum of three times until no visible particulate remains. Particulate adhering to the brush will be rinsed with methanol/ammonium hydroxide into the same container. The container will be sealed.
4. The volume of liquid collected in the first condensate trap will be measured, the value recorded, and the contents poured into a polyethylene container.
5. All train components between the filter exit and the first condensate trap will be rinsed with methanol/ammonium hydroxide. The solvent rinse will be placed in a separate polyethylene container and sealed.
6. The volume of liquid in the impingers one, two, and second condensate trap will be measured, the values recorded, and sample will be placed in the same container as step 4 above and sealed.
7. The two impingers, condensate trap, and connectors will be rinsed with methanol/ammonium hydroxide. The solvent sample will be placed in a separate polyethylene container and sealed.
8. The silica gel in the final impinger will be weighed and the weight gain value recorded.
9. Site (reagent) blank samples of the methanol/ammonium hydroxide, XAD resin, filter and distilled water will be retained for analysis.

Each container will be labeled to clearly identify its contents. The height of the fluid level will be marked on the container of each liquid sample to provide a reference point for a leakage check during transport. All samples will be maintained cool.

During each test campaign, a M-0010 blank train will be setup near the test location, leak checked (twice) and recovered along with the respective sample train. Following sample recovery, all samples will be transported to the TestAmerica Inc. for sample extraction and analysis.

See Figure 4-2 for a schematic of the M-0010 sample recovery process.



**FIGURE 4-2**  
**HFPO DIMER ACID SAMPLE RECOVERY PROCEDURES FOR METHOD 0010**

### 4.2.3 EPA Method 0010 – Sample Analysis

Method 0010 sampling trains will result in four separate analytical fractions for HFPO Dimer Acid analysis according to SW-846 Method 3542:

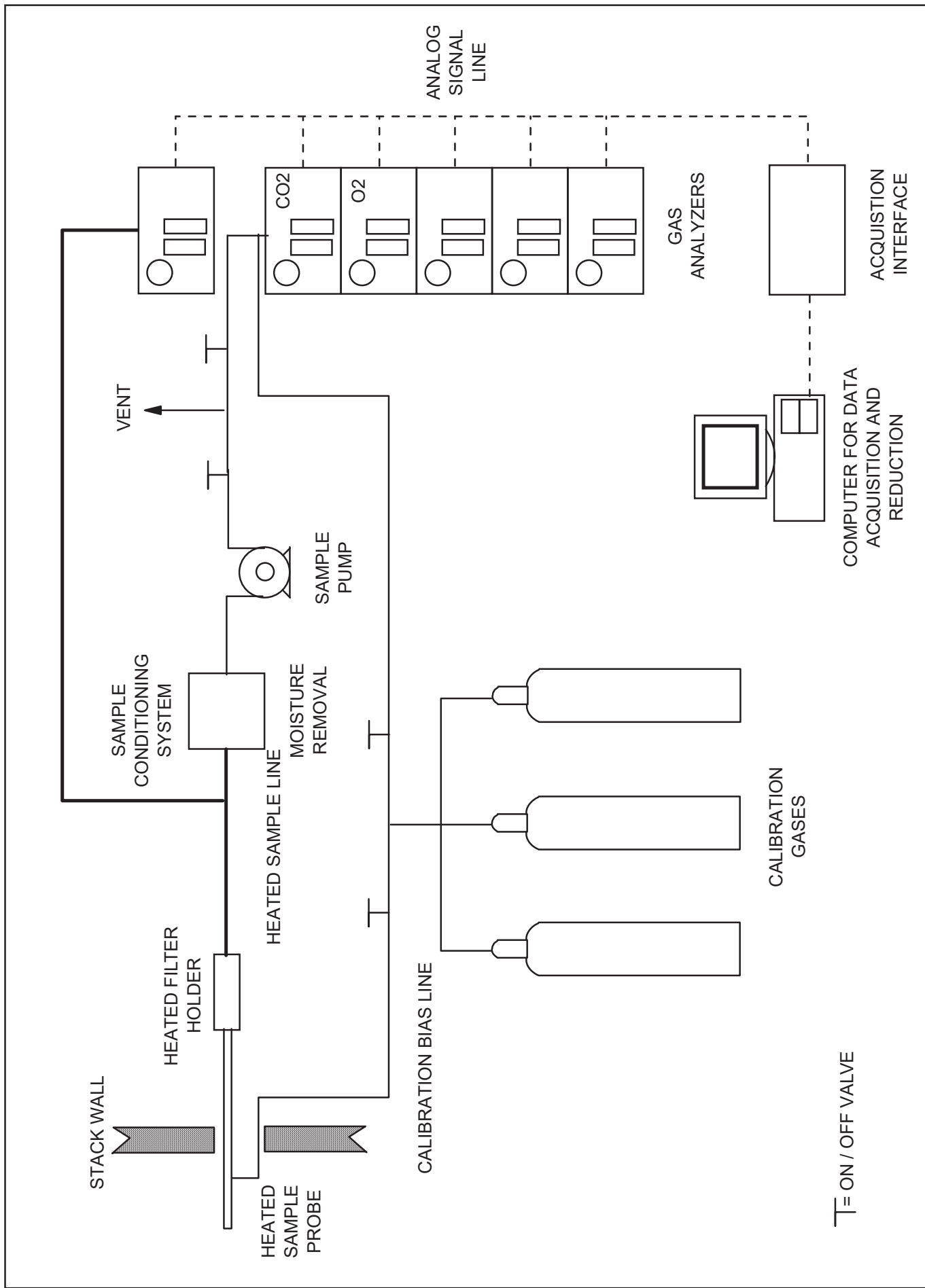
- Front-Half Composite—comprised of the Particulate Filter, and the probe, nozzle, and front-half of the filter holder solvent rinses,
- Back-half Composite—comprised of the first XAD-2 resin material and the back-half of the filter holder with connecting glassware solvent rinses,
- Condensate Composite—comprised of the aqueous condensates and the contents of Impingers #1 and 2 with solvent rinses,
- Breakthrough XAD-2 Resin Tube—comprised of the resin tube behind the series of impingers.

The second XAD-2 resin material will be analyzed separately to evaluate any possible sampling train HFPO-DA breakthrough.

The Front and Back-half composites and the second XAD-2 resin material will be placed in polypropylene wide-mouth bottles and tumbled with methanol containing 5% NH<sub>4</sub>OH for 18 hours. Portions of the extracts will be processed analytically for the HFPO dimer acid by Liquid Chromatography and dual mass spectroscopy (HPLC/MS/MS). The Condensate composite will be concentrated onto a solid phase extraction (SPE) cartridge followed by desorption from the cartridge using methanol. Portions of those extracts will also be processed analytically by HPLC/MS/MS.

Samples will be spiked with isotope dilution internal standard (IDA) at the commencement of their preparation to provide accurate assessments of the analytical recoveries. Final data will be corrected for IDA standard recoveries.

Test America has developed detailed procedures for the sample extraction and analysis for HFPO Dimer Acid. These procedures are incorporated into this test protocol in Appendix A.



**FIGURE 4-3**  
**WESTON SAMPLING SYSTEM**



### 4.3 GAS COMPOSITION

A mobile laboratory equipped with instrumental analyzers will be used to measure carbon dioxide (CO<sub>2</sub>), and oxygen (O<sub>2</sub>) concentrations. A diagram of the WESTON sampling system is presented in Figure 4-3.

A heated stainless steel probe will be used to collect a sample at the approximate centroid of each stack. At the end of the probe, a tee will permit the introduction of calibration gas. The sample will be drawn through a heated Teflon® sample line to the sample conditioner. The output from the sampling system will be recorded electronically, and one-minute averages will be recorded and displayed on a data logger. As an option, the sample may be collected at the exhaust of the Method 0010 sampling system.

Each analyzer will be set up and calibrated internally by introduction of calibration gas standards directly to the analyzer from a calibration manifold. The calibration manifold is designed with an atmospheric vent to release excess calibration gas and maintains the calibration at ambient pressure. The direct calibration sequence will consist of alternate injections of zero and mid-range gases with appropriate adjustments until the desired responses are obtained. The high range standards will then be introduced in sequence without further adjustment.

The sample line integrity will be verified by performing a bias test before and after each test period. The sampling system bias test consists of introducing the zero gas and one up range calibration standard in excess to the valve at the probe end when the system is sampling normally. The excess calibration gas flows out through the probe to maintain ambient sampling system pressure. Calibration gas supply is regulated to maintain constant sampling rate and pressure. Instrument bias check response will be compared to internal calibration responses to insure sample line integrity and to calculate a bias correction factor after each run using the ratio of the measured concentration of the bias gas certified by the calibration gas supplier.

The oxygen and carbon dioxide content of each stack gas will be measured according to EPA Method 3A procedures which incorporate the latest updates of EPA Method 7E. A Servomex Model 4900 analyzer (or equivalent) will be used to measure oxygen content. A Servomex Model 4900 analyzer (or equivalent) will be used to measure carbon dioxide content of the stack gas. Both analyzers will be calibrated with EPA Protocol gases prior to the start of the test program and performance will be verified by sample bias checks before and after each test run.

## 5. TEST PROCEDURES

Each test will be a minimum of 180 minutes in duration and sufficient to collect  $\geq 3\text{m}^3$  (105.9 ft<sup>3</sup>) of sample volume. A total of three test runs per location will be performed.

Note that if preliminary analytical results require significant sample dilution to bring the HFPO Dimer Acid concentration within instrument calibration, the sample time and sample volume may be reduced. This will require the approval of the North Carolina Department of Environmental Quality (NC DEQ).

## 6. TEST REPORT FORMAT

A written final report will be prepared for NC DEQ. The report will be submitted within 90 days of test completion. The test report will include:

1. A summary section which will contain a concise description of the Emissions Test program including reasons for testing, number and types of tests, technical approach, etc. A summary table showing key test data and results.
2. A description of the test locations and sampling equipment used for the tests.
3. A description or reference of sampling and analytical procedures.
4. Test data and results summary tables. Emissions will be reported on a concentration basis (lb/dscf, ug/m<sup>3</sup>) and mass basis (lb/hr, gm/sec).
5. A discussion section will include comments concerning any unusual process conditions or difficulties experienced with testing or analytical procedures.
6. Appendices containing:
  - Process operations data (process operating and control data to be monitored and supplied by Chemours).
  - Raw and reduced test data.
  - Laboratory analytical report.
  - Sample calculations.
  - Equipment calibration records.
  - List of project participants.

## **7. QUALITY ASSURANCE AND CALIBRATIONS**

The following procedures will be followed to insure that the emissions data collected during this test program are of high quality.

### **7.1 VELOCITY/VOLUMETRIC FLOW RATE QC PROCEDURES**

Volumetric flow rates will be determined using EPA Methods 1 and 2. The following QC steps will be followed during these tests:

- The pitot tube will be visually inspected before sampling.
- Both legs of the pitot tube will be leak-checked before sampling.
- The manometer oil will be leveled and zeroed before each run and periodically checked.
- Cyclonic flow checks using an S-type pitot tube will be performed once per source during testing.
- Pitot tube coefficients will be determined based on physical measurement techniques as delineated in Method 2.

### **7.2 MOISTURE CONTENT AND SAMPLE VOLUME QC PROCEDURES**

Gas stream moisture will be determined by EPA Method 4 as part of the M-0010 isokinetic stack tests. The following QC procedures will be followed in determining the volume of moisture collected:

- The amount of moisture collected will be determined either volumetrically or gravimetrically.
- The balance will be calibrated daily.
- The balance zero will be checked and re-zeroed if necessary before each weighing.
- The balance will be leveled and placed in a clean, motionless environment for weighings.
- The indicating silica gel will be fresh for each run and periodically inspected and replaced during runs if needed.

The QC procedures that are followed in regard to accurate sample gas volume determination will be:

- The dry gas meter will be fully calibrated annually using an EPA-approved intermediate standard device.
- Pre-test, port-change, and post-test leak-checks will be completed (must be less than 0.02 cubic feet per minute (cfm) or 4% of the average sample rate).
- The gas meter will be read to the thousandth of a cubic foot for all initial and final readings.
- Readings of the dry gas meter, meter orifice pressure (Delta H) and meter temperatures will be taken at every sampling point.
- Accurate barometric pressures will be recorded at least once per day.
- Pre- and post-test program dry gas meter checks will be completed to verify the accuracy of the meter calibration constant (Y).

### **7.3 METHOD 0010 SAMPLING QC PROCEDURES**

The specific sampling QC procedures which will ensure representative collection of Method 0010 data are as follows:

- Pre-clean sample and recovery glassware as described in Method 0010.
- The XAD-2 resin material used to collect these samples has been lot tested for HFPO-DA background. Media checks and various blanks will provide ongoing indicators of resin continued cleanliness and its appropriate storage condition.
- Only nanograde or equivalent solvents and reagents will be used for test train preparation and recovery. High purity distilled water will be used.
- The sample rate must be within 10% of the true isokinetic (100%) rate.
- All sampling nozzles will be manufactured and calibrated according to EPA standards.
- Maintain the XAD-2 resin gas stream inlet and silica gel exit gas stream temperature at or below 68 °F during testing.
- Complete recovery procedures in a clean environment.

- Maintain solvent, XAD and filter samples cool following collection and prior to analysis.
- All calculations will be double-checked for accuracy and completeness.
- All manual test apparatus will be leak checked before and after each test run. Each leak check will be recorded on a field sampling data sheet.

## 7.4 INSTRUMENTAL ANALYZER QC SAMPLING PROCEDURES

The following QC procedures will be applied to ensure collection of representative test data.

- The gas composition sampling systems (probe to sample conditioner) will be leak-checked prior to the testing.
- All analyzers will be calibrated prior to testing to ensure precise and accurate data. Protocol standards will be used to calibrate each of the analyzers. Each analyzer will be calibrated at three to four points (zero, mid, and high range) depending on reference method requirements. Nitrogen will be used to set the instrument zero. The calibration standards will be approximately 40-60 and 100% span for CO<sub>2</sub> and O<sub>2</sub>.
- Prior to formal testing, a stratification check will be performed on each stack. Per Section 8.1.2 of EPA Method 7E, a three point CO<sub>2</sub> or O<sub>2</sub> stratification check passing through the centroidal area of the stack will be performed. The three points (16.7, 50 and 83.3) percent of the stack diameter will each be sampled a minimum of two times the system response. If the CO<sub>2</sub> or O<sub>2</sub> concentration at each point in comparison to the mean difference is no more than  $\pm 5.0$  percent, then all sampling will be performed at a single point at the stack midpoint. If the difference is between 5 percent but not greater than 10 percent, a three point traverse per run will be performed. A difference of greater than 10 percent in concentration will result in performing a twelve point traverse with points calculated per EPA Method 1.
- Pre- and post-test calibration bias tests will be performed for each test run. The bias check will be performed with the calibration standard that is closest to the observed concentration in the sample gas. The average pre/post-test bias drift will not exceed 3 % of full scale.
- A permanent data record of analyzer responses will be recorded using computer software.
- If preliminary measurements of O<sub>2</sub> and CO<sub>2</sub> indicate that the stack gas concentrations are equivalent to ambient air (20.9% O<sub>2</sub>, 0% CO<sub>2</sub>), then further O<sub>2</sub> and CO<sub>2</sub> monitoring may not be required.

## **7.5 DECONTAMINATION PROCEDURES**

Stack gas sampling equipment will be pre-cleaned following standard source test method procedures. All stack gas sampling equipment will be cleaned on-site as part of individual sample recovery procedures.

Sample containers are purchased from a vendor. The vendor provides a certificate indicating that each lot of bottles is free of contaminants.

All personnel associated with sample collection will use designated personal protective equipment (PPE). Personnel will follow standard PPE decontamination procedures for each level of PPE required.

Personnel have received the proper hazardous materials training specified in 29 CFR 1910.

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**APPENDIX A**  
**TEST AMERICA PROCEDURES FOR SAMPLE EXTRACTION AND**  
**ANALYSIS OF HFPO DIMER ACID**

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## TestAmerica HFPO-DA Method 0010 Sampling Train Fraction Preparation and Analysis Summary

The Method 0010 Sampling train fractions are transported from the Chemours Plant site in Fayetteville, NC to the TestAmerica Laboratory in Knoxville, TN for processing. The fractions are collected and recovered from the sampling train according to SW-846 additional guidelines found in Method 3542 for the breakdown of Method 0010 components. The train fraction designations are as follows:

- Front-Half Composite—consisting of a particulate filter, and a probe, nozzle and front portion of the filter holder bell housing glassware solvent rinses,
- Back-Half Composite—consisting of an XAD-2 resin module, and the back portion of the filter holder bell housing with connecting glassware solvent rinses,
- Condensate and Impinger Contents—consisting of the D.I. Water content used to initially charge the impingers and Condensate collected during the sampling run.
- Breakthrough XAD-2 Resin Tube—consisting of a standard XAD-2 module placed behind the Condensate Impingers as a final quality assurance indicator of the lack of breakthrough of the HFPO-DA through the sampling train.

In the laboratory, the Front-Half sample fraction components are placed in to an HDPE bottle and spiked with  $^{13}\text{C}_3$ -HFPO isotope dilution internal standard (IDA). This composite is extracted with basic methanol for 18 hours at room temperature followed by acidification using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA. Instrumental analysis for these extracts is conducted in the TestAmerica Denver Laboratory.

The Back-Half sample fraction components, including the approximately 40 grams of XAD-2 resin material, are transferred to an HDPE bottle and spiked with the IDA internal standard. This Back-Half Composite is extracted at room temperature using two (2) successive 18 hour periods and separate portions of basic methanol. The XAD-2 resin material is removed, and the extraction fluid is acidified using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA in the TestAmerica Denver Laboratory.

The Condensate Composite fraction of the sampling train is measured to record the total volume in the composite followed by preparation by concentration on a solid phase extractor (SPE). The SPE cartridge is treated with water/methanol mixture to release the HFPO-DA. The extract is run for the HFPO-DA using Method 8321A.

The Breakthrough XAD-2 Resin Tube fraction is prepared and analyzed by the same process as that used for the Back-half sampling train fraction.

Due to the sensitivity of the LCMS methodology, concentrations levels collected on Method 0010 sampling trains of HFPO-DA may require significant dilutions in order to report analytical data that is “hard quantified” within the calibration range of the process. The diluted samples avoid “E” (estimated) values for the results of the HFPO-DA.

## **4. SAMPLING AND ANALYTICAL METHODS**

### **4.1 STACK GAS SAMPLING PROCEDURES**

The purpose of this section is to describe the stack gas emissions sampling trains and to provide detail of the stack sampling and analytical procedures utilized during the emissions test program.

#### **4.1.1 Pre-Test Determinations**

Preliminary test data will be obtained at each test location. Stack geometry measurements will be measured and recorded, and traverse point distances verified. A preliminary velocity traverse will be performed utilizing a calibrated "S" type pitot tube and an inclined manometer to determine velocity profiles. Flue gas temperatures will be observed with a calibrated direct readout panel meter equipped with a chromel-alumel thermocouple. Preliminary water vapor content will be measured by performance of an EPA Method 4 moisture test or by wet bulb/dry bulb temperature measurements.

A check for the presence or absence of cyclonic flow will be conducted at each test location.

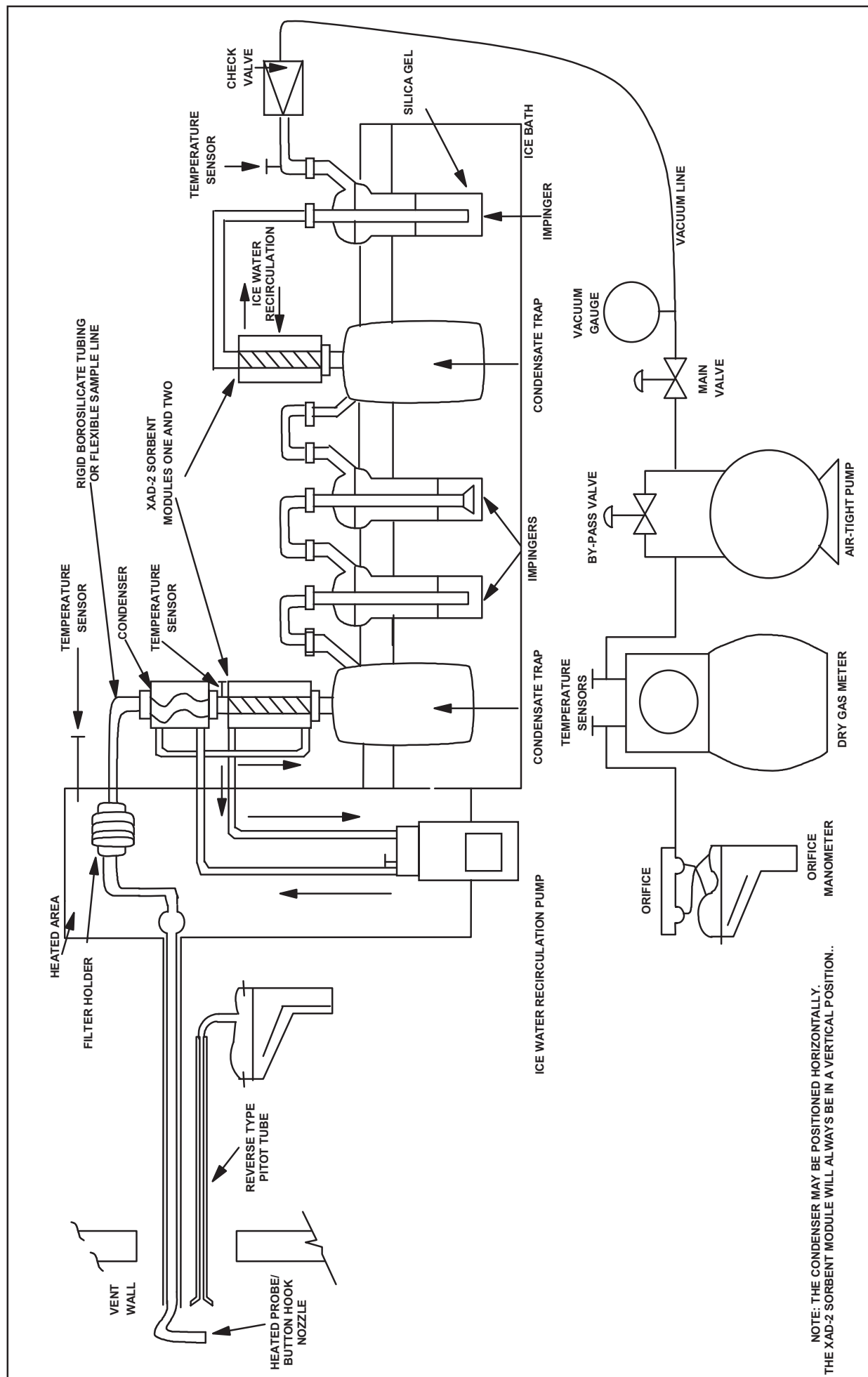
Preliminary test data will be used for nozzle sizing and sampling rate determinations for isokinetic sampling procedures.

Calibration of probe nozzles, pitot tubes, metering systems, and temperature measurement devices will be as specified in Section 5 of EPA Method 5 test procedures.

### **4.2 STACK PARAMETERS**

#### **4.2.1 EPA Method 0010**

The sampling train utilized to perform the HFPO Dimer Acid sampling will be an EPA Method 0010 train (see Figure 4-1). The Method 0010 consists of a borosilicate or stainless steel nozzle that will be attached directly to a heated borosilicate probe. In order to minimize possible thermal degradation of the HFPO Dimer Acid, the probe and particulate filter will be heated above stack temperature to minimize water vapor condensation before the filter. The probe will be connected directly to a heated borosilicate filter holder containing a solvent extracted glass fiber filter.



**FIGURE 4-1**  
**EPA METHOD 0010 SAMPLING TRAIN**

A section of borosilicate glass or flexible polyethylene tubing will connect the filter holder exit to a Graham (spiral) type ice water-cooled condenser, an icewater-jacketed sorbent module containing approximately 40 grams of XAD-2 resin. The XAD-2 resin tube is equipped with an inlet temperature sensor. The XAD-2 resin trap will be followed by a condensate knockout impinger and a series of two impingers containing 100-ml of high purity distilled water. The train will also include a second XAD-2 resin trap behind the impinger section to evaluate possible sampling train breakthrough. Each XAD-2 resin trap will be connected to a 1-L condensate knockout trap. The final impinger will contain 300 grams of dry pre-weighed silica gel. All impingers and the condensate traps will be maintained in an ice bath. Ice water will be continuously circulated in the condenser and both XAD-2 modules to maintain method required temperature. A control console with a leakless vacuum pump, a calibrated orifice, and dual inclined manometers will be connected to the final impinger via an umbilical cord to complete the sample train.

During sampling, gas stream velocities will be measured by attaching a calibrated "S"-type pitot tube into the gas stream adjacent to the sampling nozzle. The velocity pressure differential will be observed immediately after positioning the nozzle at each traverse point, and the sampling rate adjusted to maintain isokineticity  $\pm 10$ . Flue gas temperature will be monitored at each point with a calibrated panel meter and thermocouple. Isokinetic test data will be recorded at each traverse point during all test periods, as appropriate. Leak checks will be performed on the sampling apparatus according to reference method instructions, prior to and following each run, component change (if required) or during midpoint port changes.

#### **4.2.2 EPA Method 0010 Sample Recovery**

At the conclusion of each test, the sampling train will be dismantled, the openings sealed, and the components transported to the field laboratory trailer for recovery.

A consistent procedure will be employed for sample recovery:

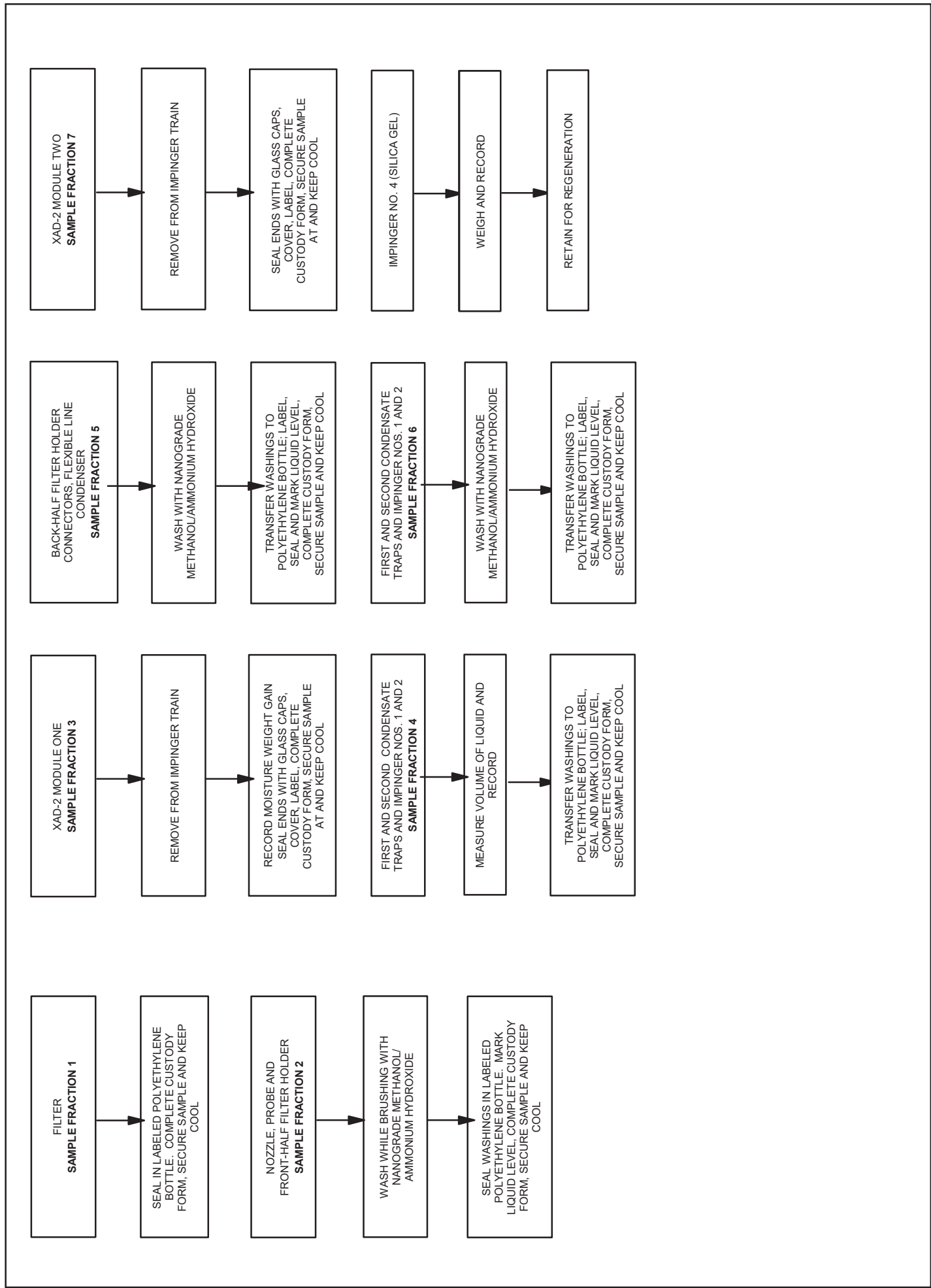
1. The two XAD-2 covered (to minimize light degradation) sorbent modules (1 and 2) will be sealed and labeled.

2. The glass fiber filter(s) will be removed from the holder with tweezers and placed in a polyethylene container along with any loose particulate and filter fragments.
3. The particulate adhering to the internal surfaces of the nozzle, probe and front half of the filter holder will be rinsed with a solution of methanol and ammonium hydroxide into a polyethylene container while brushing a minimum of three times until no visible particulate remains. Particulate adhering to the brush will be rinsed with methanol/ammonium hydroxide into the same container. The container will be sealed.
4. The volume of liquid collected in the first condensate trap will be measured, the value recorded, and the contents poured into a polyethylene container.
5. All train components between the filter exit and the first condensate trap will be rinsed with methanol/ammonium hydroxide. The solvent rinse will be placed in a separate polyethylene container and sealed.
6. The volume of liquid in the impingers one, two, and second condensate trap will be measured, the values recorded, and sample will be placed in the same container as step 4 above and sealed.
7. The two impingers, condensate trap, and connectors will be rinsed with methanol/ammonium hydroxide. The solvent sample will be placed in a separate polyethylene container and sealed.
8. The silica gel in the final impinger will be weighed and the weight gain value recorded.
9. Site (reagent) blank samples of the methanol/ammonium hydroxide, XAD resin, filter and distilled water will be retained for analysis.

Each container will be labeled to clearly identify its contents. The height of the fluid level will be marked on the container of each liquid sample to provide a reference point for a leakage check during transport. All samples will be maintained cool.

During each test campaign, a M-0010 blank train will be setup near the test location, leak checked (twice) and recovered along with the respective sample train. Following sample recovery, all samples will be transported to the TestAmerica Inc. for sample extraction and analysis.

See Figure 4-2 for a schematic of the M-0010 sample recovery process.



**FIGURE 4-2**  
**HFPO DIMER ACID SAMPLE RECOVERY PROCEDURES FOR METHOD 0010**

### 4.2.3 EPA Method 0010 – Sample Analysis

Method 0010 sampling trains will result in four separate analytical fractions for HFPO Dimer Acid analysis according to SW-846 Method 3542:

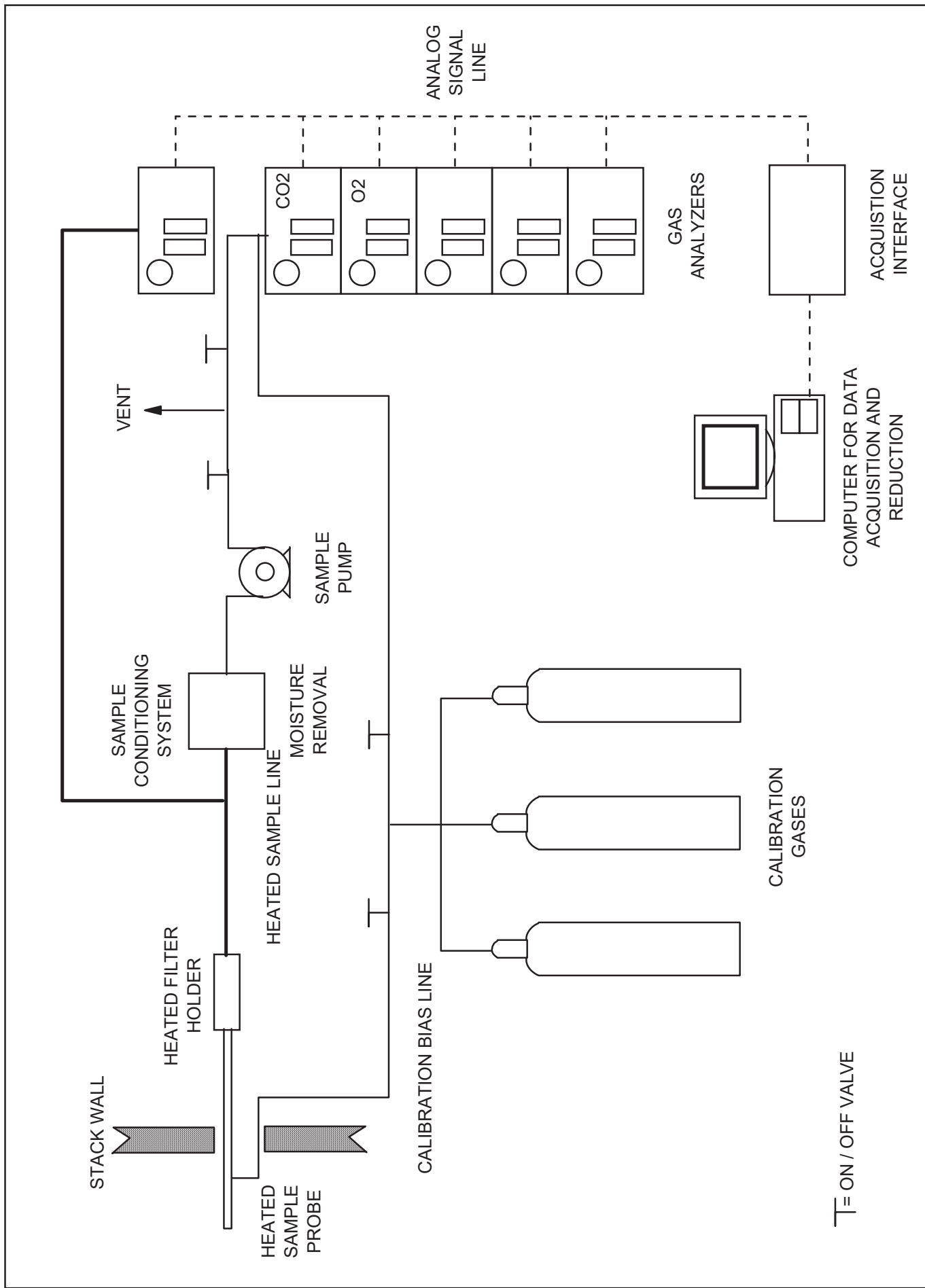
- Front-Half Composite—comprised of the Particulate Filter, and the probe, nozzle, and front-half of the filter holder solvent rinses,
- Back-half Composite—comprised of the first XAD-2 resin material and the back-half of the filter holder with connecting glassware solvent rinses,
- Condensate Composite—comprised of the aqueous condensates and the contents of Impingers #1 and 2 with solvent rinses,
- Breakthrough XAD-2 Resin Tube—comprised of the resin tube behind the series of impingers.

The second XAD-2 resin material will be analyzed separately to evaluate any possible sampling train HFPO-DA breakthrough.

The Front and Back-half composites and the second XAD-2 resin material will be placed in polypropylene wide-mouth bottles and tumbled with methanol containing 5% NH<sub>4</sub>OH for 18 hours. Portions of the extracts will be processed analytically for the HFPO dimer acid by Liquid Chromatography and dual mass spectroscopy (HPLC/MS/MS). The Condensate composite will be concentrated onto a solid phase extraction (SPE) cartridge followed by desorption from the cartridge using methanol. Portions of those extracts will also be processed analytically by HPLC/MS/MS.

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Test America has developed detailed procedures for the sample extraction and analysis for HFPO Dimer Acid. These procedures are incorporated into this test protocol in Appendix A.



**FIGURE 4-3**  
**WESTON SAMPLING SYSTEM**



### 4.3 GAS COMPOSITION

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A heated stainless steel probe will be used to collect a sample at the approximate centroid of each stack. At the end of the probe, a tee will permit the introduction of calibration gas. The sample will be drawn through a heated Teflon® sample line to the sample conditioner. The output from the sampling system will be recorded electronically, and one-minute averages will be recorded and displayed on a data logger. As an option, the sample may be collected at the exhaust of the Method 0010 sampling system.

Each analyzer will be set up and calibrated internally by introduction of calibration gas standards directly to the analyzer from a calibration manifold. The calibration manifold is designed with an atmospheric vent to release excess calibration gas and maintains the calibration at ambient pressure. The direct calibration sequence will consist of alternate injections of zero and mid-range gases with appropriate adjustments until the desired responses are obtained. The high range standards will then be introduced in sequence without further adjustment.

The sample line integrity will be verified by performing a bias test before and after each test period. The sampling system bias test consists of introducing the zero gas and one up range calibration standard in excess to the valve at the probe end when the system is sampling normally. The excess calibration gas flows out through the probe to maintain ambient sampling system pressure. Calibration gas supply is regulated to maintain constant sampling rate and pressure. Instrument bias check response will be compared to internal calibration responses to insure sample line integrity and to calculate a bias correction factor after each run using the ratio of the measured concentration of the bias gas certified by the calibration gas supplier.

The oxygen and carbon dioxide content of each stack gas will be measured according to EPA Method 3A procedures which incorporate the latest updates of EPA Method 7E. A Servomex Model 4900 analyzer (or equivalent) will be used to measure oxygen content. A Servomex Model 4900 analyzer (or equivalent) will be used to measure carbon dioxide content of the stack gas. Both analyzers will be calibrated with EPA Protocol gases prior to the start of the test program and performance will be verified by sample bias checks before and after each test run.

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3. A description or reference of sampling and analytical procedures.
4. Test data and results summary tables. Emissions will be reported on a concentration basis (lb/dscf, ug/m<sup>3</sup>) and mass basis (lb/hr, gm/sec).
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6. Appendices containing:
  - Process operations data (process operating and control data to be monitored and supplied by Chemours).
  - Raw and reduced test data.
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  - Equipment calibration records.
  - List of project participants.

## **7. QUALITY ASSURANCE AND CALIBRATIONS**

The following procedures will be followed to insure that the emissions data collected during this test program are of high quality.

### **7.1 VELOCITY/VOLUMETRIC FLOW RATE QC PROCEDURES**

Volumetric flow rates will be determined using EPA Methods 1 and 2. The following QC steps will be followed during these tests:

- The pitot tube will be visually inspected before sampling.
- Both legs of the pitot tube will be leak-checked before sampling.
- The manometer oil will be leveled and zeroed before each run and periodically checked.
- Cyclonic flow checks using an S-type pitot tube will be performed once per source during testing.
- Pitot tube coefficients will be determined based on physical measurement techniques as delineated in Method 2.

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Gas stream moisture will be determined by EPA Method 4 as part of the M-0010 isokinetic stack tests. The following QC procedures will be followed in determining the volume of moisture collected:

- The amount of moisture collected will be determined either volumetrically or gravimetrically.
- The balance will be calibrated daily.
- The balance zero will be checked and re-zeroed if necessary before each weighing.
- The balance will be leveled and placed in a clean, motionless environment for weighings.
- The indicating silica gel will be fresh for each run and periodically inspected and replaced during runs if needed.

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- The dry gas meter will be fully calibrated annually using an EPA-approved intermediate standard device.
- Pre-test, port-change, and post-test leak-checks will be completed (must be less than 0.02 cubic feet per minute (cfm) or 4% of the average sample rate).
- The gas meter will be read to the thousandth of a cubic foot for all initial and final readings.
- Readings of the dry gas meter, meter orifice pressure (Delta H) and meter temperatures will be taken at every sampling point.
- Accurate barometric pressures will be recorded at least once per day.
- Pre- and post-test program dry gas meter checks will be completed to verify the accuracy of the meter calibration constant (Y).

### **7.3 METHOD 0010 SAMPLING QC PROCEDURES**

The specific sampling QC procedures which will ensure representative collection of Method 0010 data are as follows:

- Pre-clean sample and recovery glassware as described in Method 0010.
- The XAD-2 resin material used to collect these samples has been lot tested for HFPO-DA background. Media checks and various blanks will provide ongoing indicators of resin continued cleanliness and its appropriate storage condition.
- Only nanograde or equivalent solvents and reagents will be used for test train preparation and recovery. High purity distilled water will be used.
- The sample rate must be within 10% of the true isokinetic (100%) rate.
- All sampling nozzles will be manufactured and calibrated according to EPA standards.
- Maintain the XAD-2 resin gas stream inlet and silica gel exit gas stream temperature at or below 68 °F during testing.
- Complete recovery procedures in a clean environment.

- Maintain solvent, XAD and filter samples cool following collection and prior to analysis.
- All calculations will be double-checked for accuracy and completeness.
- All manual test apparatus will be leak checked before and after each test run. Each leak check will be recorded on a field sampling data sheet.

## 7.4 INSTRUMENTAL ANALYZER QC SAMPLING PROCEDURES

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- The gas composition sampling systems (probe to sample conditioner) will be leak-checked prior to the testing.
- All analyzers will be calibrated prior to testing to ensure precise and accurate data. Protocol standards will be used to calibrate each of the analyzers. Each analyzer will be calibrated at three to four points (zero, mid, and high range) depending on reference method requirements. Nitrogen will be used to set the instrument zero. The calibration standards will be approximately 40-60 and 100% span for CO<sub>2</sub> and O<sub>2</sub>.
- Prior to formal testing, a stratification check will be performed on each stack. Per Section 8.1.2 of EPA Method 7E, a three point CO<sub>2</sub> or O<sub>2</sub> stratification check passing through the centroidal area of the stack will be performed. The three points (16.7, 50 and 83.3) percent of the stack diameter will each be sampled a minimum of two times the system response. If the CO<sub>2</sub> or O<sub>2</sub> concentration at each point in comparison to the mean difference is no more than  $\pm 5.0$  percent, then all sampling will be performed at a single point at the stack midpoint. If the difference is between 5 percent but not greater than 10 percent, a three point traverse per run will be performed. A difference of greater than 10 percent in concentration will result in performing a twelve point traverse with points calculated per EPA Method 1.
- Pre- and post-test calibration bias tests will be performed for each test run. The bias check will be performed with the calibration standard that is closest to the observed concentration in the sample gas. The average pre/post-test bias drift will not exceed 3 % of full scale.
- A permanent data record of analyzer responses will be recorded using computer software.
- If preliminary measurements of O<sub>2</sub> and CO<sub>2</sub> indicate that the stack gas concentrations are equivalent to ambient air (20.9% O<sub>2</sub>, 0% CO<sub>2</sub>), then further O<sub>2</sub> and CO<sub>2</sub> monitoring may not be required.

## **7.5 DECONTAMINATION PROCEDURES**

Stack gas sampling equipment will be pre-cleaned following standard source test method procedures. All stack gas sampling equipment will be cleaned on-site as part of individual sample recovery procedures.

Sample containers are purchased from a vendor. The vendor provides a certificate indicating that each lot of bottles is free of contaminants.

All personnel associated with sample collection will use designated personal protective equipment (PPE). Personnel will follow standard PPE decontamination procedures for each level of PPE required.

Personnel have received the proper hazardous materials training specified in 29 CFR 1910.

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**APPENDIX A**  
**TEST AMERICA PROCEDURES FOR SAMPLE EXTRACTION AND**  
**ANALYSIS OF HFPO DIMER ACID**

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- Front-Half Composite—consisting of a particulate filter, and a probe, nozzle and front portion of the filter holder bell housing glassware solvent rinses,
- Back-Half Composite—consisting of an XAD-2 resin module, and the back portion of the filter holder bell housing with connecting glassware solvent rinses,
- Condensate and Impinger Contents—consisting of the D.I. Water content used to initially charge the impingers and Condensate collected during the sampling run.
- Breakthrough XAD-2 Resin Tube—consisting of a standard XAD-2 module placed behind the Condensate Impingers as a final quality assurance indicator of the lack of breakthrough of the HFPO-DA through the sampling train.

In the laboratory, the Front-Half sample fraction components are placed in to an HDPE bottle and spiked with  $^{13}\text{C}_3$ -HFPO isotope dilution internal standard (IDA). This composite is extracted with basic methanol for 18 hours at room temperature followed by acidification using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA. Instrumental analysis for these extracts is conducted in the TestAmerica Denver Laboratory.

The Back-Half sample fraction components, including the approximately 40 grams of XAD-2 resin material, are transferred to an HDPE bottle and spiked with the IDA internal standard. This Back-Half Composite is extracted at room temperature using two (2) successive 18 hour periods and separate portions of basic methanol. The XAD-2 resin material is removed, and the extraction fluid is acidified using formic acid. The final formulation is filtered through a 0.45  $\mu\text{m}$  filter and analyzed by Method 8321A for HFPO-DA in the TestAmerica Denver Laboratory.

The Condensate Composite fraction of the sampling train is measured to record the total volume in the composite followed by preparation by concentration on a solid phase extractor (SPE). The SPE cartridge is treated with water/methanol mixture to release the HFPO-DA. The extract is run for the HFPO-DA using Method 8321A.

The Breakthrough XAD-2 Resin Tube fraction is prepared and analyzed by the same process as that used for the Back-half sampling train fraction.

Due to the sensitivity of the LCMS methodology, concentrations levels collected on Method 0010 sampling trains of HFPO-DA may require significant dilutions in order to report analytical data that is “hard quantified” within the calibration range of the process. The diluted samples avoid “E” (estimated) values for the results of the HFPO-DA.

## Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas

### Sampling and Field Procedure for the Evaluation of Fluoroether E-1 in Stack Gas

Sample Name: Modified Method 18 Midget Impinger Sampling Method

Sampler: Stack Sampling Specialists

Sampling Locations: Stack Sampling Platform

Sampling & Health & Safety Equipment: Sampling apparatus and safety equipment recommendations are as follows:

- Method 18 Midget Impinger Sampling Train (See schematic)
- HDPE 60 ml sample bottles with screw-top caps
- Purge and Trap Grade Methanol for Impinger charges and glassware rinses
- Clean or New HDPE squirt bottles
- Safety glasses or face shield
- Latex Gloves and other site specific safety equipment as required
- Dry Ice / Methanol Bath for chilling the impinger train

Sampling Strategy and Design: The target analyte for this sampling campaign is Fluoroether E-1, CAS # 3330-15-2). This compound is classified as a volatile boiling point compound (40°C) and can be trapped into methanol charged impingers chilled in a dry ice /methanol bath. The final Fluoroether E-1 train-total concentration determined by this sampling train will be the sum of the following analytical fractions:

$$[\text{Total } \mu\text{g in Impinger \#1}] + [\text{Total } \mu\text{g in Impinger \#2}] + [\text{Total } \mu\text{g in Impinger \#3}] + [\text{Total } \mu\text{g in Impinger \#4}] + [\text{Total } \mu\text{g in Impinger \#5}] + [\text{Total } \mu\text{g in Impinger \#6}] = \text{Train Total } \mu\text{g of E-1 for the Sampling Run}$$

Sample Collection Rates: Stack gas collections are conducted continuously at a nominal rate of 0.25 Liters/minute during the sampling run for 60 minutes of sampling time or longer. A greater number of minutes may be required to include specific batch operations or specific process campaigns within the plant operations. Inherently low stack gas concentrations of Fluoroether E-1 may also require longer sampling times in order to evaluate the concentrations detectable by the analytical methodology employed. Breakthrough to the last impinger will be a concern at some point, therefore slow sampling coupled with the maintenance of the dry ice train chilling are essential operational targets.

The intact sampling train is sealed and removed from the stack sampling platform to the train recovery area. Following removal to the sampling trailer the various train components are collected in individual 60 mL HDPE vials.

## **Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)**

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Each 60 minute (or greater) complete sampling train collection constitutes a Sampling Run under these conditions. Three (3) complete sampling runs will complete a test condition.

### **Sampling Procedures:**

The preparation of Modified Method 18 Train glassware, probes, and connecting glassware should incorporate a thorough cleaning and rinsing of these components with Purge and Trap grade methanol. Glass components should be baked in an oven at 100 °C for 2 hours followed by a final methanol rinse. Any tubing used during the sample collections to connect the sampling probe to the impinger train should be new, and receive an initial methanol rinse before the test commences.

Persons handling the midget impinger train components should don latex gloves. Fresh gloves should be worn during each separate stage of train handling to avoid the transfer of contamination to the train.

A strict approach should be taken toward the quarantine of essential personnel and equipment used during the collection of Fluoroether E-1 samples to avoid contamination of these samples.

Storage and handling of train components and samples are required to be done in a clean sampling trailer or lab space. Solvents like toluene, methylene chloride, and acetone have the potential to severely cross contaminate the Modified Method 18 samples unless deliberate care is taken to prevent exposure to these solvents.

The midget impingers and connecting glassware should be protected from contamination by placing them in separate clean coolers during shipping and storage at the sampling locations.

Modified Method 18 Impinger Train Operation -- The sample collection procedure set-up generally follows standard EPA protocols. The dry gas meter will be calibrated before arriving at the test site, and the sample train components will be cleaned and assembled before charging the midget impingers with Purge and Trap grade methanol. The train will be leak tested at approximately 10 inches of Hg using a system isolation valve that prevents exposure of the train to possible contamination in the ambient air during the leak check. Leak tests will be conducted before and after the sampling interval for each run.

Before the run is commenced, all six (6) impingers are charged with 15 - 20 mls of methanol. The impinger train will be set into a dry ice / methanol bath for the duration of sample collection. The sampling train should be submerged in the dry ice / methanol bath to a level where the methanol level in each impingers are slightly below the ice bath external fluid level to maximize the cooling efficiency of the methanol. The analyte being collected during this stack emissions characterization is Fluoroether E-1 (CAS # 3330-15-2) whose boiling Point = 40°C. Under these operating conditions the Fluoroether E-1 analyte efficiently traps and is isolated for analysis in the impinger methanol. Once the E-1 is dissolved in the methanol, the handling of the samples is expected to be relatively easy to maintain.

## **Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)**

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The probe of the sampling train will be inserted into an appropriate sampling port and purged with stack gas to fill the dead volume of the train before the actual sampling is started. The Fluoroether E-1 sample collection is a non-isokinetic process so a single point probe location is set. The probe will be heated to a few degrees above the stack gas temperatures to prevent the condensation of moisture in the probe during the run. The stack gas will be sampled at a rate of 0.25 L/min for  $\geq 60$  minutes to collect a nominal sample volume of  $\geq 15$  L for each run.

At the completion of the sampling run on the stack, the sampling train will be disconnected from the probe assembly and capped. The assembled train will be secured in a carriage or cooler, and moved to the sampling trailer for the completion of the train breakdown process. A cleaned or new HDPE squirt bottle should be used for all probe and glassware rinses. A squirt bottle previously used with any solvent other than Purge and Trap grade methanol should be avoided. The probe assembly and connecting glassware receive triple methanol rinses and the rinsates will be placed into the labelled sample container used for the collection of Impinger #1 contents.

The contents of Midget Impinger #1 will be placed into the 60 ml HDPE sample container clearly labeled with the run number and impinger number. The impinger will be triple rinsed with small aliquots of methanol and the rinses are added to the container. The probe and connecting tubing will also receive methanol rinses that are placed in with the Impinger #1 sample fraction. Using a clean (or new) HDPE squirt bottle the probe and all related connecting glassware are rinsed into the Impinger #1 sample container. Three (3) small volumes of methanol should be sufficient to effectively rinse the train components.

Midget Impinger #2 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

Midget Impinger #3 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

Midget Impinger #4 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

Midget Impinger #5 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

Midget Impinger #6 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

After collecting the samples, the Methanol impinger samples will be placed in Ziploc<sup>®</sup> bags and stored in coolers on dry ice.

## **Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)**

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During a sampling run, a complete blank train will be set up to simulate the handling of the actual test samples. The Methanol will remain in an identical train for the approximate length of time required to complete a sampling run. The beginning and end leak checks will be performed on the blank train, and the probe will be heated to the standard operating temperature. Samples will be recovered from the blank train by the same operator and in the same location as those for the standard runs.

Samples will be placed on dry ice in clean coolers, which will be stored in an area away from other samples and potential sources of contamination.

### **Laboratory Analysis:**

The analytical laboratory will conduct screening level analyses followed by analyses of the Modified Method 18 Methanol impinger samples by SW-846 Method 8260B. Generally, a 10ul portion of the impinger sample is placed into the purge and trap device of the instrument. Method 8260 surrogate compounds and internal standards are added to the portions of the samples processed. For low level samples, the portion of the original sample added is increased to a 100ul portion placed onto the purge and trap device. The higher injection portions are considered after sample screening is completed and if sample loadings are below the calibration range of the instrument. Dilutions of samples may also be required for highly concentrated impinger samples. For very low concentrations of E-1 in samples, selective ion monitoring (SIM) will be employed to quantify the target analyte.

### **Quality Control/Quality Assurance Requirements:**

A train blank set of Modified Method 18 samples will be collected one time during each test campaign. The train blank will be assembled and placed near the stack sampling location for the duration of one sampling run. The blank train will be leak checked at the beginning and end of the sampling period.

A methanol trip blank and reagent blank will be included with all modified Method 18 samples sent to the analytical laboratory.

Samples are to be stored on dry ice from the time they are collected from the impinger glassware and placed into sampling bottles.

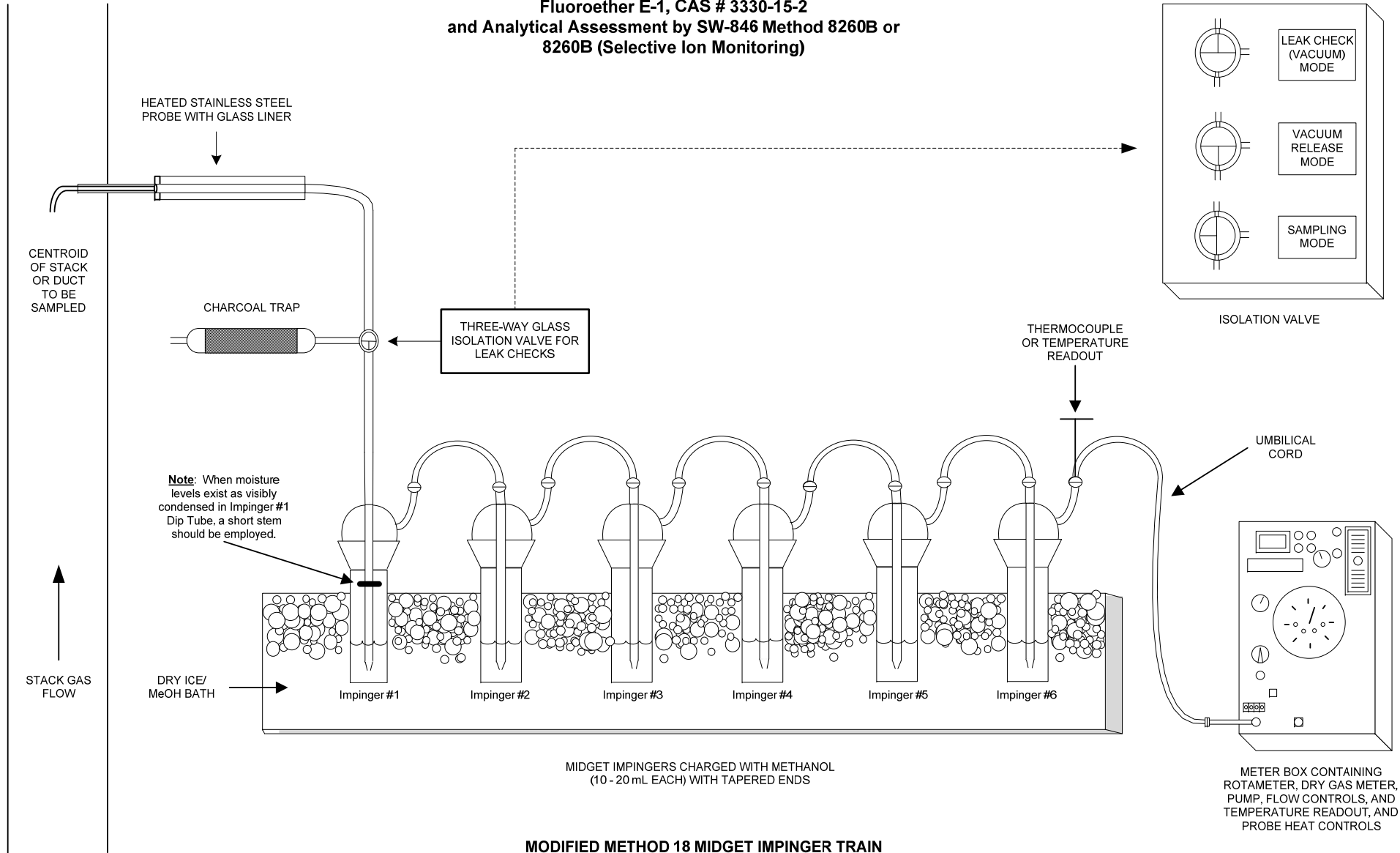
Holding Times: All samples are to be analyzed within 14 days of collection.

### **Method References:**

Modified Method 18 – "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography." EPA 40 CFR Part 60, Appendix A.

Method 8260 - "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)". Taken from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, September 1986 and its updates. USEPA, OSWER, Washington, D.C. 20460.

**Schematic of Modified Method 18 Sampling Train for Sampling  
Fluoroether E-1, CAS # 3330-15-2  
and Analytical Assessment by SW-846 Method 8260B or  
8260B (Selective Ion Monitoring)**



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## Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas

### Sampling and Field Procedure for the Evaluation of Fluoroether E-1 in Stack Gas

Sample Name:	Modified Method 18 Midget Impinger Sampling Method
Sampler:	Stack Sampling Specialists
Sampling Locations:	Stack Sampling Platform
Sampling & Health & Safety Equipment:	<p>Sampling apparatus and safety equipment recommendations are as follows:</p> <ul style="list-style-type: none"> <li>• Method 18 Midget Impinger Sampling Train (See schematic)</li> <li>• HDPE 60 ml sample bottles with screw-top caps</li> <li>• Purge and Trap Grade Methanol for Impinger charges and glassware rinses</li> <li>• Clean or New HDPE squirt bottles</li> <li>• Safety glasses or face shield</li> <li>• Latex Gloves and other site specific safety equipment as required</li> <li>• Dry Ice / Methanol Bath for chilling the impinger train</li> </ul>
Sampling Strategy and Design:	<p>The target analyte for this sampling campaign is Fluoroether E-1, CAS # 3330-15-2). This compound is classified as a volatile boiling point compound (40°C) and can be trapped into methanol charged impingers chilled in a dry ice /methanol bath. The final Fluoroether E-1 train-total concentration determined by this sampling train will be the sum of the following analytical fractions:</p> $[\text{Total } \mu\text{g in Impinger \#1}] + [\text{Total } \mu\text{g in Impinger \#2}] + [\text{Total } \mu\text{g in Impinger \#3}] + [\text{Total } \mu\text{g in Impinger \#4}] + [\text{Total } \mu\text{g in Impinger \#5}] + [\text{Total } \mu\text{g in Impinger \#6}] = \text{Train Total } \mu\text{g of E-1 for the Sampling Run}$
Sample Collection Rates:	<p>Stack gas collections are conducted continuously at a nominal rate of 0.25 Liters/minute during the sampling run for 60 minutes of sampling time or longer. A greater number of minutes may be required to include specific batch operations or specific process campaigns within the plant operations. Inherently low stack gas concentrations of Fluoroether E-1 may also require longer sampling times in order to evaluate the concentrations detectable by the analytical methodology employed. Breakthrough to the last impinger will be a concern at some point, therefore slow sampling coupled with the maintenance of the dry ice train chilling are essential operational targets.</p> <p>The intact sampling train is sealed and removed from the stack sampling platform to the train recovery area. Following removal to the sampling trailer the various train components are collected in individual 60 mL HDPE vials.</p>

## Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)

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Each 60 minute (or greater) complete sampling train collection constitutes a Sampling Run under these conditions. Three (3) complete sampling runs will complete a test condition.

### Sampling Procedures:

The preparation of Modified Method 18 Train glassware, probes, and connecting glassware should incorporate a thorough cleaning and rinsing of these components with Purge and Trap grade methanol. Glass components should be baked in an oven at 100 °C for 2 hours followed by a final methanol rinse. Any tubing used during the sample collections to connect the sampling probe to the impinger train should be new, and receive an initial methanol rinse before the test commences.

Persons handling the midget impinger train components should don latex gloves. Fresh gloves should be worn during each separate stage of train handling to avoid the transfer of contamination to the train.

A strict approach should be taken toward the quarantine of essential personnel and equipment used during the collection of Fluoroether E-1 samples to avoid contamination of these samples.

Storage and handling of train components and samples are required to be done in a clean sampling trailer or lab space. Solvents like toluene, methylene chloride, and acetone have the potential to severely cross contaminate the Modified Method 18 samples unless deliberate care is taken to prevent exposure to these solvents.

The midget impingers and connecting glassware should be protected from contamination by placing them in separate clean coolers during shipping and storage at the sampling locations.

Modified Method 18 Impinger Train Operation -- The sample collection procedure set-up generally follows standard EPA protocols. The dry gas meter will be calibrated before arriving at the test site, and the sample train components will be cleaned and assembled before charging the midget impingers with Purge and Trap grade methanol. The train will be leak tested at approximately 10 inches of Hg using a system isolation valve that prevents exposure of the train to possible contamination in the ambient air during the leak check. Leak tests will be conducted before and after the sampling interval for each run.

Before the run is commenced, all six (6) impingers are charged with 15 - 20 mls of methanol. The impinger train will be set into a dry ice / methanol bath for the duration of sample collection. The sampling train should be submerged in the dry ice / methanol bath to a level where the methanol level in each impingers are slightly below the ice bath external fluid level to maximize the cooling efficiency of the methanol. The analyte being collected during this stack emissions characterization is Fluoroether E-1 (CAS # 3330-15-2) whose boiling Point = 40°C. Under these operating conditions the Fluoroether E-1 analyte efficiently traps and is isolated for analysis in the impinger methanol. Once the E-1 is dissolved in the methanol, the handling of the samples is expected to be relatively easy to maintain.



## **Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)**

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The probe of the sampling train will be inserted into an appropriate sampling port and purged with stack gas to fill the dead volume of the train before the actual sampling is started. The Fluoroether E-1 sample collection is a non-isokinetic process so a single point probe location is set. The probe will be heated to a few degrees above the stack gas temperatures to prevent the condensation of moisture in the probe during the run. The stack gas will be sampled at a rate of 0.25 L/min for  $\geq 60$  minutes to collect a nominal sample volume of  $\geq 15$  L for each run.

At the completion of the sampling run on the stack, the sampling train will be disconnected from the probe assembly and capped. The assembled train will be secured in a carriage or cooler, and moved to the sampling trailer for the completion of the train breakdown process. A cleaned or new HDPE squirt bottle should be used for all probe and glassware rinses. A squirt bottle previously used with any solvent other than Purge and Trap grade methanol should be avoided. The probe assembly and connecting glassware receive triple methanol rinses and the rinsates will be placed into the labelled sample container used for the collection of Impinger #1 contents.

The contents of Midget Impinger #1 will be placed into the 60 ml HDPE sample container clearly labeled with the run number and impinger number. The impinger will be triple rinsed with small aliquots of methanol and the rinses are added to the container. The probe and connecting tubing will also receive methanol rinses that are placed in with the Impinger #1 sample fraction. Using a clean (or new) HDPE squirt bottle the probe and all related connecting glassware are rinsed into the Impinger #1 sample container. Three (3) small volumes of methanol should be sufficient to effectively rinse the train components.

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Midget Impinger #5 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

Midget Impinger #6 will be collected with its associated glassware rinses in a separate 60ml HDPE vial. This fraction will be analyzed separately for the target analyte.

After collecting the samples, the Methanol impinger samples will be placed in Ziploc<sup>®</sup> bags and stored in coolers on dry ice.

## **Modified Method 18 Midget Impinger Method for Determination of Fluoroether E-1 Emissions in Stack Gas (Continued)**

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During a sampling run, a complete blank train will be set up to simulate the handling of the actual test samples. The Methanol will remain in an identical train for the approximate length of time required to complete a sampling run. The beginning and end leak checks will be performed on the blank train, and the probe will be heated to the standard operating temperature. Samples will be recovered from the blank train by the same operator and in the same location as those for the standard runs.

Samples will be placed on dry ice in clean coolers, which will be stored in an area away from other samples and potential sources of contamination.

### **Laboratory Analysis:**

The analytical laboratory will conduct screening level analyses followed by analyses of the Modified Method 18 Methanol impinger samples by SW-846 Method 8260B. Generally, a 10ul portion of the impinger sample is placed into the purge and trap device of the instrument. Method 8260 surrogate compounds and internal standards are added to the portions of the samples processed. For low level samples, the portion of the original sample added is increased to a 100ul portion placed onto the purge and trap device. The higher injection portions are considered after sample screening is completed and if sample loadings are below the calibration range of the instrument. Dilutions of samples may also be required for highly concentrated impinger samples. For very low concentrations of E-1 in samples, selective ion monitoring (SIM) will be employed to quantify the target analyte.

### **Quality Control/Quality Assurance Requirements:**

A train blank set of Modified Method 18 samples will be collected one time during each test campaign. The train blank will be assembled and placed near the stack sampling location for the duration of one sampling run. The blank train will be leak checked at the beginning and end of the sampling period.

A methanol trip blank and reagent blank will be included with all modified Method 18 samples sent to the analytical laboratory.

Samples are to be stored on dry ice from the time they are collected from the impinger glassware and placed into sampling bottles.

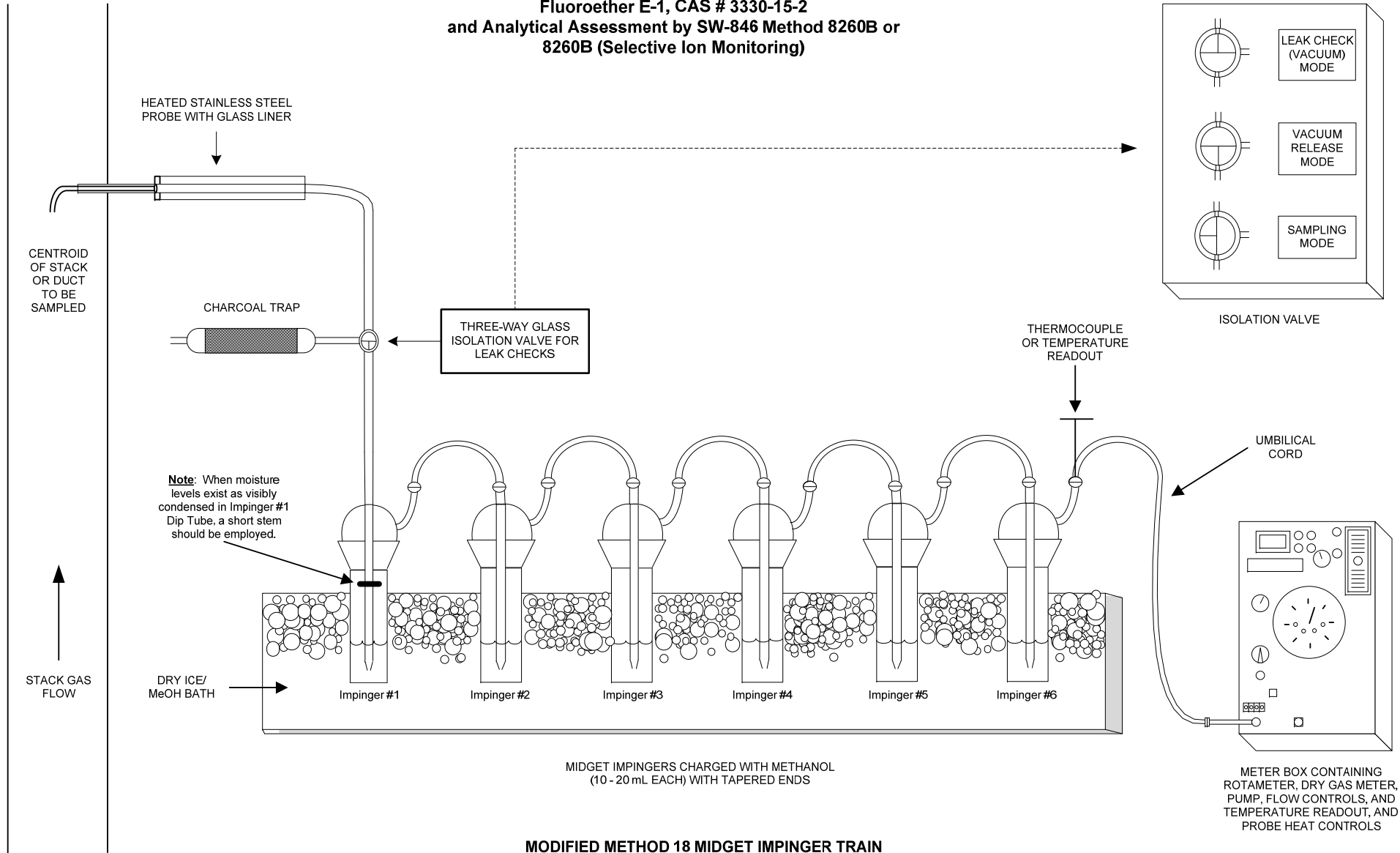
Holding Times: All samples are to be analyzed within 14 days of collection.

### **Method References:**

Modified Method 18 – "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography." EPA 40 CFR Part 60, Appendix A.

Method 8260 - "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)". Taken from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, September 1986 and its updates. USEPA, OSWER, Washington, D.C. 20460.

**Schematic of Modified Method 18 Sampling Train for Sampling  
Fluoroether E-1, CAS # 3330-15-2  
and Analytical Assessment by SW-846 Method 8260B or  
8260B (Selective Ion Monitoring)**



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